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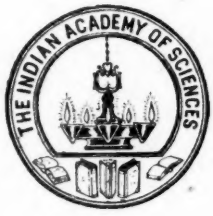

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SEISMOLOGICAL FEATURES OF THE SATPURA EARTHQUAKE OF THE 14TH MARCH 1938

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Received March 3, 1942
(Communicated by Dr. K. R. Ramanathan)

Summary

An earthquake of moderate strength occurred in the early morning of March 14, 1938 in the Satpura range. For its magnitude, the area over which the shock was felt was unusually large, about 400,000 sq. miles. It is estimated that a maximum surface intensity between VII and VIII in the modified Mercalli scale of 1931 was reached near the epicentre. The isoseismals of this earthquake were roughly elliptical with the long axis in an approximately north-south direction. It is probable that the earthquake was connected with a fault line in the Satpuras. From the seismological data of near stations, the position of the epicentre is calculated as 21° 32′ N. and 75° 50′E. and the time of origin as $0^h48^m30^s$ G.M.T. The depth of focus is calculated as 40 km. These determinations are supported by macroseismic data and observations of P, P′ and pP at distant stations. The magnitude of the shock was about 5·5 and energy about 10^{19} Ergs. Velocities of the various crustal waves which are identifiable in the Indian seismograms are given. Thickness of the granitic layer (including the sedimentary one) is tentatively calculated as 40 km. and that of the basaltic one as 10 km. These values agree with those observed for the Eastern Alps region. The shock apparently originated near the bottom of the granitic layer. Some of the seismograms of this shock recorded at the Indian stations are reproduced.

Introduction

A moderately strong earthquake occurred in the Satpuras near Khandwa on the early morning (6^h19^m I.S.T.) of March 14, 1938. This shook the whole of Central India and Western India including Gujarat, the major part of the Central Provinces and part of Rajputana, Kathiawar and the Hyderabad State. It was reported that the shock was felt as far as Delhi on the north and Belgaum on the south. On the east and west, the limits of the felt area do not appear to have extended much beyond Seoni and Bhavnagar, respectively. A hot spring which had been in existence near Chopda for more than 100 years was reported to have disappeared after the shock. Taking into consideration all the non-instrumental reports, the boundary of the felt area was roughly elliptical in shape with the long axis in north-south direction and included an area of about 390,000 sq. miles.

From the seismological data obtained at the Indian observatories and Ceylon, the epicentre of the earthquake is located at 21° 32′ N. and 75° 50′E. in the Satpura range. This point is almost central with respect to the following places at which the reported intensity was greatest; Maheshwar in Indore to the north, Khandwa to the northeast, Chopda near Jalgaon to the southwest and Bhusawal to the south. The shock occurred at 0^h48^m 30^s G.M.T. It is probable that the earthquake is connected with a fault in the Satpura range.[1]

2. Object of the study.—The study of the various aspects of this earthquake is interesting from the fact that earthquakes are very rare in this part of India. This earthquake appears to have been the strongest of all the shocks which affected this particular region in historic times. Secondly, this is the only earthquake regarding which satisfactory instrumental data from 5 Indian stations within about 11° of epicentral distance and with good locations of observing stations with respect to the epicentre, are available.

3. Previous shocks in this region.—On May 27, 1847, a shock occurred in the Narbada valley at the foot of a hill called the Dumohpahari. A tremendous noise and rumbling in the hill was heard. This was supposed to have been due to a landslip but was found not to be so. In the morning the hill was reported to have been rent for about threefourths of a mile and engulfed trees of great size.[2*]

On November 18, 1863, another shock occurred. This took place in Nimar and Barwani country and was reported to have been accompanied by a loud noise like the trampling of a multitude of horses. In the Barwani country, walls fell. The direction of movement was from NW to SE. It was felt on the southern side of the Narbada river from Barwani on the west to Poonassa in the east and on the north of the river from Manpoor to Barwani, but was not noticed to the south of the Satpura range.[3*]

In recent years a few minor tremors are reported to have been felt around the Satpuras. Of these the one which occurred on July 20, 1935, was of slight intensity. This was recorded at 7^h 42^m G.M.T. by the seismographs at Bombay and felt at Baroda, Surat and Kapadbari. It is believed to have originated in the Tapti valley.

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*T. Oldham, *Mem. Geol. Surv. Ind.*, Vol. XIX, part 3. The second shock is included in the "Catalogue of destructive earthquakes by Milne, B.A. Reports, 1911" but not the first one. The information regarding the second earthquake appears to be more certain than about the first one and its origin seems to have been near the present Satpura range shock. Further lists of epicentres by Milne and Miss Bellamy in the Index Catalogue of epicentres for 1913-1930 do not give any other shock in this region. After 1930, the Bombay records are more or less complete.

The present shock was felt at Bombay. The Bombay seismograms showed that the first movement was impulsive and very clear in both the N and E components. The amplitudes as read on the seismograms were 1·6 mm to south and 3·0 mm to west. Coupled with the telegraphic information about the times of arrival of some phases at Agra and Calcutta this gave the approximate position of the epicentre to be 3°·7 away from Bombay and situated to the southwest of Indore in Central India.

4. Issue of circular asking for information.—With a view to collect more detailed information, a circular letter was sent from Bombay to a number of places round about the epicentre. In response to this circular, 36 replies were received. Besides these, 3 more reports were received from voluntary observers. These 39 reports were supplemented by information collected at Poona[4] from observers and at Bombay from press reports. In all, intensities caused by this earthquake could be estimated at about 60 stations. 25 more stations reported as having felt the shock but the information given was not enough to estimate the intensity at these places.

5. Distribution of Intensity.—The intensities were estimated in the modified Mercalli scale of 1931, suggested by Wood and Neumann[5]; and have been roughly shown by drawing isoseismal lines in a map, Fig. 1. So far

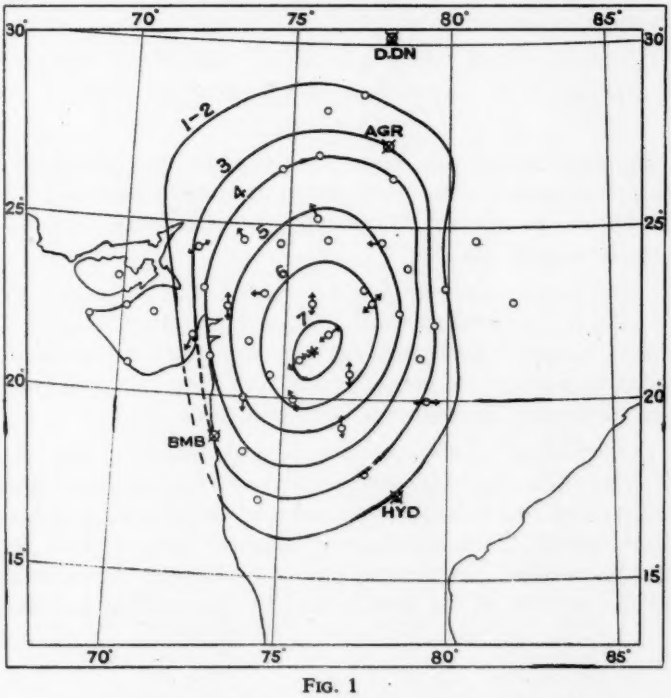


FIG. 1

Isoseismals of Satpura Earthquake of March 14th, 1938

as the available reports indicate, the maximum intensity 7 of this scale was reached at 4 places. It appears that at Maheshwar and Chopda intensities 7 or even more were experienced. These places are almost equidistant (40–50 miles) from the epicentre. Report from no other station nearer the epicentre is available. This may be partly due to the fact that the epicentral region is hilly. It is therefore possible that an intensity greater than 7 might have been manifested at some place nearer the epicentre. On the whole the shock was more strongly felt on alluvium than on solid rock at equal epicentral distances. From the fact that the shock occurred in the early morning when many people were awake rather than at night and from the nature of available reports, the outer limit of the felt area may be considered to have been fairly well represented by the outermost isoseismal line in the map. It may be noted that Barmer which is not very far from the outer boundary of the felt area, reported an intensity for which a value of 6 in R.F. scale was estimated at Poona. The data on which this estimation is based are not available to us. On the other side, it was reported that the shock was not felt at Jubbulpore, Sutna and Pendra Road. In spite of some of the apparently discordant observations mentioned above, the form of the isoseismal lines indicates that on the whole the shock was felt fairly uniformly over a large area and that the fall of intensity away from the epicentral tract was more or less uniform.

6. *Direction of earth-motion and Sound.*—Directions of earth-motion were estimated at 16 places and have been marked by arrows in the intensity map.

Underground sound was heard at Khandwa and Malegaon. Noise " like that of a passing train " was heard at Freelandganj and " like that of an aeroplane " at Jalgoan. Apparently this phenomenon did not extend beyond the isoseismal line 5.

7. *Seismograms available for the study.*—The original seismograms from Agra (N,E), Hyderabad (N,E), Dehra Dun (N), Calcutta (N) and a copy of the Colombo seismiogram (E) were available for this study. Kodaikanal failed to register the shock as the recording light was weak. The data from 22 foreign observatories were also used.

8. *Determination of the epicentre from seismological data from near stations.*—As a preliminary step, the S-P intervals from Bombay, Hyderabad, Agra, Dehra Dun and Calcutta were used and the epicentral distances were found from Jeffreys' 'Table for the near eathquake pulses, 1937'. With these stations as centres and Δ's as radii, arcs of circles were drawn on a suitable map and the centroid of the area formed by intersections was assumed to

be the epicentre. Distances with respect to this epicentre were then calculated from the formula 2 Versin $\Delta = (a\text{-}A)^2 + (b\text{-}B)^2 + (c\text{-}C)^2$. Observed times of P_n were next plotted against these calculated distances. The same process was continued for different trial positions and the one corresponding to which the times of P_n of the above stations lay on a straight line was adopted as the correct position of the epicentre. The co-ordinates of such position are 21° 32′ N. and 75° 50′ E., in the Satpura range. Travel-time curves of P_n and S_n with respect to this position of the epicentre and the stations having epicentral distances lying between 3°·9 and 15°·1 are reproduced in Fig. 2. Curves relating to the other phases identifiable in the Indian seismograms are also reproduced in the same figure.

9. P and P′ observations from distant stations.—Available P and P′ observations at 22 distant stations and also macroseismic data appear to support this position of the epicentre. It should, however, be noted that the distant stations are not uniformly distributed round the epicentre. The residuals of P against Jeffreys' continental surface-focus times[6] after correcting them for the adopted depth of focus (40 km.), for this earthquake are given in Table I. The P′ residuals against Gutenberg and Richter's tables[7] are also given in brackets.

TABLE I

Station	Distance in degrees	Po		O–C secs.
		m.	s.	
Tashkent	20·6	4	36	− 1·0
Baku	29·0	5	56	− 0·1
Grozny	33·15	6	37	4·3
Erivan	34·37	6	47	3·7
Ekaterinburg	37·03	7	07	1·1
Kasara	37·2	7	14	6·7
Helwan	40·7	7	40	1·6
Moscow	44·4	8	09	2·4
Pulkovo	49·8	8	51	1·9
Beograd	50·7	8	57·5	1·6
Chur	58·4	9	52·2	0·0
Hamburg	58·6	9	54	0·4
St. Gart	58·7	9	54·5	0·2
Zurich	59·1	9	56·8	− 0·3
Strasburg	59·7	10	01	− 0·2
Neuchâtel	60·2	10	04·4	− 0·3
Paris	63·13	10	22	− 2·4
Algiers	63·9	10	29	− 0·4
Kew	64·8	10	36	0·7
Granada	69·03	11	01	− 1·0
Mt. Wilson	122·7	18	56	(− 3)
Riverside	123·1	18	57	(− 3)

10. Time correction.—Comparision of the origin times computed from the observed times of P_n at Dehra Dun and Culcutta with the origin time determined from all observations suggested corrections of + 14 secs. and − 13 secs. respectively at these places. When these corrections were applied uniformly to the tabulated times of all the pulses, they were in good agreement with the times of the corresponding phases at the other near stations.

11. Time of origin.—The time of occurrence of the shock is obtained as $0^h48^m30^s$ G.M.T. from the data of near stations. This is also calculated from the available *p*P observations from Sohon's formula $\frac{p\mathrm{P}+\mathrm{P}}{2}-t_0$ where *p*P and P denote the observed times of *p*P and P and t_0 the travel time of P from a surface focus to the observing station.[8] Such calculations give for Stuttgart ($\Delta = 58°\cdot7$), $0^h48^m29^s\cdot3$ and for Kew ($\Delta = 64°\cdot8$), $0^h48^m30^s\cdot8$. The mean is $0^h48^m30^s$, that is, the same as the time obtained from the data of near stations. It would be seen from Table I, that P and P′ observations at distant stations also suggest the same origin time.

12. Depth of focus.—The area over which the earthquake was felt is abnormally large. Secondly, the decrease of intensity away from the epicentre is not as rapid as it should be in the case of a shallow earthquake. These considerations suggested at the outset that the depth of focus of this earthquake was greater than normal (about 10 km.). The following is the further evidence for the depth of focus.

(1) From *p*P: Both Kew and Stuttgart recorded an impulsive phase 11 secs. after *i*P. Assuming this to be *p*P we get 44 km. for the value of the depth from Stuttgart and 37 km. from Kew.

(2) From P-O: If the data of Kasara, Grozny and Erivan which show large residuals are rejected, the data of the remaining stations in Table I suggest a value of about 40 km. for the depth of focus.

(3) From P′-O: Riverside and Mt. Wilson each gives about 50 km. for the depth.

(4) From macroseismic observations: The depth of focus of an earthquake is related to the maximum observed intensity at different distances from the epicentre. A formula connecting these quantities due to Blake,[9] is $\mathrm{J}-j=-s\log\cos e$ where J is the maximum intensity of the shock, j is the intensity of a chosen isoseismal of radius Rj and h is the depth of focus, $e=\tan^{-1}\frac{\mathrm{R}j}{h}$ and s is an empirical parameter which has a value of

about 5·35. Putting J=about 8, j =2 (both on Mercalli scale) and R= 560 km., $\frac{Rj}{h}$ would be 13 and h about 43 km.

(5) From the mean rate of fall of surface intensity: A curve can be drawn to indicate the mean rate of fall of surface intensity due to an earthquake with increase of epicentral distance.[10] When such a curve in R.F. scale was drawn for the Satpura range earthquake and compared with a similar curve available for the north Tazima (Japan) earthquake of which the depth was otherwise determined to be 30 km.[11] the nature of departure of the slopes of the two curves pointed to a depth near about 40 km. in the case of the former.

40 km. is therefore adopted as being the most probable value for the depth of focus of the Satpura range eathquake.

13. Magnitude and Energy.— From the maximum horizontal amplitudes of ground we get 5·5 as the magnitude from which the energy comes out to be about 10^{19} Ergs for this earthquake.[12]

14. Seismograms.—Seismograms of the Satpura earthquake recorded at Bombay, Hyderabad, Agra and Calcutta are reproduced in Fig. 2. At Bombay, the record was lost for about a minute after the incidence of the phase marked 3. At Hyderabad, the amplitudes following the phase marked 4 were quite large. Part of them were not recorded and part recorded faintly. The phase marked 4 is recorded very clearly with a large amplitude in all the seismograms except Bombay where the record was lost at about the expected time of arrival of this phase. The phase 3 is also prominent at Hyderabad and Calcutta and though of small amplitude, is identifiable at Dehra Dun but absent at Agra. The phases 1 and 2 are clear with large amplitudes at Bombay and with small amplitudes at Hyderabad and Agra. The corresponding movements at Dehra Dun are quite small. In view of the types of instruments and time-scales used these phases could not perhaps be expected to be recorded much better than in the present instance. It is to be added that a weak emergent movement precedes S_n at Agra, Dehra Dun and Calcutta by 5 to 7 secs. The phase identified as S_n in the Colombo seismogram (not reproduced) is the second movement following the first prominent one in the group of shear waves by 7 secs.

Velocities of the pulses.—Velocities of the different pulses tabulated from the above seismograms are given in column 1 in Table II.

TABLE II

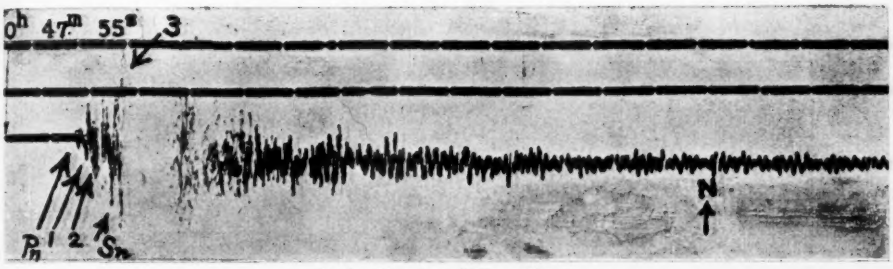
Velocity in Km./sec.		Velocity in Km./sec.	
Satpura earthquake	Obtained by different investigators	Satpura earthquake	Obtained by different investigators
(1)	(2)	(1)	(2)
7·73 (P_n) 6·44 (1) 5·47 (2)	7·7 to 8·3 (P_n) 6·3 to 6·8 (P*) 5·4 to 5·8 ($\bar{P}$)	4·38 (S_n) 3·66 (3) 3·38 (4)	4·3 to 4·5 (S_n) 3·6 to 3·7 (S*) 3·3 to 3·5 ($\bar{S}$)

In column (2) of the same table are given the velocities of P_n, P*, $\bar{P}$, S_n, S* and $\bar{S}$ respectively obtained by other investigators in different localities.[13] It appears from a comparison of these velocities that the phases marked 1, 2, 3 and 4 in the seismograms of the Satpura range earthquake correspond to P*, $\bar{P}$, S* and $\bar{S}$ respectively.

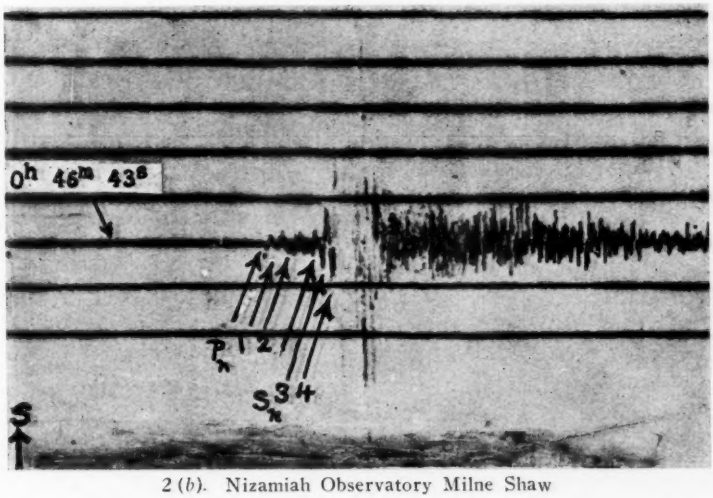
Thickness of the crustal layers.—The presence of $\bar{P}$ and $\bar{S}$ in the seismograms points to the presence of an igneous layer (called granitic layer by Jeffreys) round about the Satpuras. As the depth of focus of the shock was 40 Km., the thickness of this layer must be at least 40 Km. Using the delay of starting of S* with respect to $\bar{S}$ which is 4·5 secs., the thickness of the granitic layer (including the sedimentary one) is calculated from Jeffreys' formula[14] to be about 40 Km. Similarly, from the delay of S* and S_n, the thickness of the basaltic layer is obtained as about 10 Km. These values are found to be about the same as those obtained in respect of the Eastern Alps region. In Table III are given the values of the thickness of the crustal layers determined at different parts of the world.[15]

TABLE III

Locality	Depth of granitic layer (Km.)	Depth of continental crust (Km.)
		(Granitic + basaltic)
England	10	20
S. Germany	30	45
S. Europe	about 30	45
Caucasus	..	about 45
Central Asia region of 40°N., 70° E.	about 20	40–50
Philippine Islands	.. ..	about 50
Japan	about 20	50 decreasing towards the Pacific
Southern and Central California	15	30–40
E. Alps	40	50
Central India round about 22° N., 76° E. ..	about 40	about 50

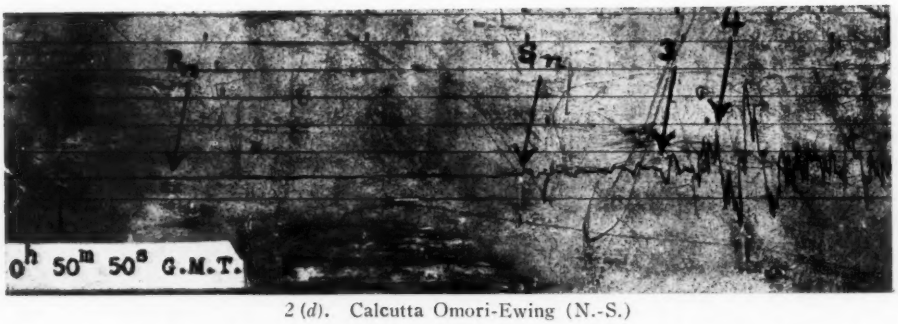


2(*a*). Bombay Milne Shaw



2(*b*). Nizamiah Observatory Milne Shaw

2 (c). Agra Omori-Ewing (N.-S.)



2 (d). Calcutta Omori-Ewing (N.-S.)

FIG. *2 (a-d).* Seismograms of the Satpura Earthquake of March 14, 1933

It is however to be remarked that considering the various uncertainties which are involved in calculating the thicknesses no precision can be claimed for these values and they are only to be taken as tentative. If the identification of $\overline{P}$ and $\overline{S}$ is correct, it would mean that the shock originated nearly at the base of the granitic layer.

The investigation was begun at the instance of Dr. K. R. Ramanathan and I am thankful to him for his interest and advice. My thanks are also due to Dr. S. R. Savur for the facilities made available to me to complete the work and to Professor B. Gutenberg who kindly sent us the readings of the Russian stations from his file.

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THE PROBLEM OF THE LAST-RESIDUE-CLASS IN THE DISTRIBUTIVE LATTICE

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(Communicated by Dr. R. Vaidyanathaswamy, M.A., D.Sc., F.A.Sc.)

Introduction

In a distributive lattice L with units (0, 1), we define a congruence relation between pairs of elements with respect to an ideal thus: the elements a, b are said to be *congruent* with respect to the α-(μ-) ideal K of L if elements x, y exist in K such that $a \cdot x = b \cdot y$ $(a + x = b + y)$. Such a congruence relation is reflexive, symmetric and transitive,* and so determines a partitioning of the lattice into non-null, disjoint "*residue-classes*" with respect to K, namely, the classes of mutually-congruent elements. That residue class which contains the unit 0 (1) of L, is called "*the last-residue-class*" of K. Evidently the element c of L will be in the last-residue-class of K if, and only if, an element d exists in K such that $c \cdot d = 0$ $(c + d = 1)$.† The first result of importance is that "*the last-residue-class of an α-ideal is a μ-ideal*" *and vice-versa*; for let a, b belong to the last-residue-class of the α-ideal K of L; then elements x, y exist in K such that $a \cdot x = 0$ and $b \cdot y = 0$. Since $x \cdot y$ is in K and $(a+b)\ x \cdot y = a \cdot x \cdot y + b \cdot x \cdot y = 0$, it follows that $a+b$ is in the last-residue-class; also, if $c < a$, then $c \cdot x = c \cdot a \cdot x = 0$, so that c is in the last-residue-class of K. This proves that the last-residue-class of an α-ideal is a μ-ideal; the dual result is proved similarly.

In this paper I try to solve the following problems relating to the last-residue-class proposed by Dr. R. Vaidyanathaswamy in the course of his departmental lectures on "lattice-theory":

(P. 1) to characterise the last-residue-class of an ideal K of L by means of ideal operations on K;

(P. 2) to determine conditions under which an ideal of L is the last-residue-class of another;

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* That it is reflexive and symmetric follow directly from the definition. To prove the transitivity, we note that, if elements p, q, r, s exist in the α-ideal K such that $a \cdot p = b \cdot q$ and $b \cdot r = c \cdot s$, where a, b, c are any elements of L, then $p \cdot r$, $s \cdot q$ are in K and satisfy the relation $a \cdot (p \cdot r) = b \cdot q \cdot r = c \cdot (s \cdot q)$.

† This follows from the relations $0 \cdot e = 0$ $(1 + e = 1)$ for all e of L, and $0 = 0 \cdot 1$ $(1 = 1 + 0)$.

(P. 3) to determine the ideals of L which are identical with the last-residue-class of their last-residue-class.

Firstly, I give, in § 1, a partial solution of (P. 3) for the general distributive lattice with units, by obtaining a sufficient condition for an ideal of L to be equal to the last-residue-class of its last-residue-class. In § 6, I solve all the problems for a Boolean Algebra by using the " Boolean complement " of an ideal as defined by Miss Pankajam.‡ Next, I obtain solutions of (P. 1) and (P. 2) for a distributive lattice in which every element has a product-complement in § 7, and for the general distributive lattice with units in § 8. For these solutions I make use of the three new concepts of " *the extension* ", " *the elementwise-complement,* " and " *the sector-ideal,* " which are studied in the sections 2 to 5.

For the fundamental properties of ideals and of product-complements in a distributive lattice, reference may be made to the papers mentioned in the Bibliography. An important result is that the sets L_μ, L_α of μ-ideals and α-ideals of a distributive lattice L are each complete lattices with all sums distributive.‡ Therefore, in each, every element has a product complement¶; and, hence, the sets N_μ, N_α of normal elements of L_μ, L_α, are Boolean Algebras and " subsystems "¶ of L_μ, L_α relative to unrestricted products.‖

For many valuable suggestions and kind criticism during the work, I am greatly indebted to Dr. R. Vaidyanathaswamy.

§ 1. *The last-residue-class of the last-residue-class.*—Let L be a general distributive lattice with, 0, 1, and S, the set of simple elements of L. Since the sum and product of simple elements are simple and when $a \in S$, an a' exists in S such that $a \cdot a' = 0$ and $a + a' = 1$, S is a Boolean Algebra and a sub-lattice of L. We first prove that

(1·1) " *any ideal of L contains the last-residue-class of its last-residue-class;*"

for, if c is in the last-residue-class of the last-residue-class of the α-ideal K of L, then elements d, e exist such that $c+d=1$, $d \cdot e = 0$, and $e \in K$; hence $c = c+d \cdot e = (c+d).(c+e) = c+e > e$, so that, since K is an α-ideal and e is in it, c is also in K; this proves the result for an α-ideal; the dual is proved similarly.

‡ See Pankajam (5) {Th. 7, 18}.

¶ See MacNeille (1) {7·6, 5·2}.

‖ See Stone (3) {Th. 29.} Stone has proved these results for the ideals of a Boolean Ring. The proof here is similar.

Next we find the relation between the intersections with S of an ideal of L and of its last-residue-class.

(1·2) " *The intersection with S of the last-residue-class of an ideal K of L is the Boolean Complement in S of the intersection of K with S.*"

For, let J be the μ-ideal of S in which the μ-ideal K of L intersects S and $\bar{J}$ the Boolean complement in S of J. Then, when $a \in J$ since $a' + a = 1$ and $a \in K$, a' is in the last-residue-class of K. Hence $\bar{J}$ is contained in the intersection of the last-residue-class of K with S; conversely, if b is an element of S in the last residue class of K, then an element c exists in K such that $b + c = 1$; hence $b' = b'(b+c) = b' \cdot b + b' \cdot c = b' \cdot c < c$, so that, since K is a μ-ideal and c is in it, b' is an element of S in K, that is, $b' \in J$; hence, as $b = (b')'$, $\bar{J}$ contains the intersection with S of the last-residue-class of K.

This completes the proof of the result for a μ-ideal; the dual is proved similarly.

As immediate corollaries to (1·2) we deduce: (1·3) " *the last-residue-class of the last-residue-class of an ideal has the same intersection with S as the ideal itself*; "

[which follows from the fact that the Boolean complement of the Boolean complement of an ideal of S is the ideal itself*]; and

(1·4) " *an ideal of L generated from a family of elements of S is equal to the last-residue-class of its last-residue-class*;"

[which follows from (1·1) and (1·3)].

We can show also that

(1·5) " *an ideal of L is simple if, and only if, it is the principal ideal generated by an element of S; and an ideal of L is the sum of simple ideals if, and only if, it is generated by a set of elements of S.*"

For, if a is in S, there is a' in S such that $a \cdot a' = 0$ and $a + a' = 1$; hence $P_\mu(a)$. $P_\mu(a') = P_\mu(0)$ and $P_\mu(a) + P_\mu(a') = P_\mu(1)$, which shows that the principal ideal $P_\mu(a)$ is simple. Conversely, if A is a simple μ-ideal, then a μ-ideal A′ exists such that $A \cdot A' = P_\mu(0)$, and $A + A' = P_\mu(1)$. Hence, if $a \in A$, and $b \in A'$, $a \cdot b = 0$; also, as $1 \in P_\mu(1)$, elements a, a' exist in A, A′ respectively such that $a + a' = 1$. As $a \in A$, $a' \in A'$, $a \cdot a' = 0$ so that a is in S and if $c \in A$, $c \cdot a' = 0$ and $c = c \cdot (a + a') = c \cdot a + c \cdot a' = c \cdot a < a$; therefore $A = P_\mu(a)$, where $a \in S$. Thus it is proved that a simple μ-ideal is a principal μ-ideal generated by an element of S;

* See Pankajam (5) {Th. 18.}

the dual is proved similarly. Next, if a μ-ideal K of L is the sum of the simple ideals $P_\mu(b_r)$, $b_r \epsilon S$, then K is generated in L from the set of elements b_r of S; and, conversely if the μ-ideal K is generated from a set (b_r) of elements of S, and if J is the μ-ideal of S generated from the set $\{b_r\}$, then K contains $\{b_r\}$ and so J, while each element of K is $<$ an element of J. Hence $K = \sum_{a \epsilon K} P_\mu(a) \subset \sum_{b \epsilon J} p\mu(b) \subset \sum_{a \epsilon K} P_\mu(a) = K$, so that $K = \sum_{b \epsilon J} P_\mu(b)$ which expresses K as the sum of simple ideals.

The dual result when K is an α-ideal is proved similarly.

From (1·4) and (1·5) we deduce

(1·6) "*if an ideal of L is the sum of simple ideals, then it is identical with the last-residue-class of its last-residue-class.*"

In (1·6) we may also replace the term "the sum of simple ideals" by the equivalent term "the extension in L of an ideal of S."*

§2. *Notation.*—In this section L, N are two distributive lattices with units, of which N is a subsystem of L relative to finite multiplication, that is, $N \subset L$, and the products in N and in L of any two elements of N are the same.

Since the ordering relation in a lattice can be defined solely in terms of lattice-multiplication, the ordering relation in N is the same as in L. As N is not a sub-lattice of L, the sums, $a \oplus b$, and $a + b$ in N and in L respectively, of the elements a, b of N, will not, in general, be the same. However we can see that $a + b > a \oplus b$, since $a \oplus b > a$ and $> b$ in N and, therefore, in L also.

The extension in L of an ideal of N

Given a μ- (α-) ideal J of N the μ-(α-) ideal of L generated from the elements of J is called "*the extension*" in L of J.

We can deduce immediately that

(2·1) "*the element c of L is in the extension in L of the μ-(α-) ideal J of N if, and only if, an element d exists in J such that $c < d$ ($c > d$).*"

For, if d is in J and $c < d$ ($c > d$), then c is in the extension of J. And, conversely, if c is in the extension of J, the finite set of elements $c_1, \ldots . c_n$ and $d = c_1 \oplus \ldots . \oplus c_n$ ($d = c_1 \ldots . . c_n$) exist in J such that $c > c_1 \oplus \ldots . \oplus c_n > c_1 + \ldots . + c_n = d$ ($c < c_1 \ldots . c_n = d$). This completes the proof of (2·1).

* See (2·91).

From (2·1) we can deduce

(2·2) "*if k is the extension of the* μ-(α-) *ideal J of N, then, whenever either of the sums* $\Sigma_{a\epsilon K}\ a$, $\Sigma_{b\epsilon J}\ b$ (*products* $\Pi_{a\epsilon K}\ a$, $\Pi_{b\epsilon J}\ b$) *exists in L, so does the other and the two are identical;*"

for since $J \subset K$, it follows from (2·1), that an element of L is $>$ ($<$) every element of K if, and only if, it is $>$ ($<$) every element of J; the result (2·2) follows directly from this.

From (2·1) and the transitivity of the ordering relation we can easily deduce that (2·3) "if *M is a subsystem relative to finite multiplication of N, so is it of L, and the extension in L of the extension in N of an ideal of M is the same as its extension in L.*"

From (2·1) we also infer the following:

(2·4) "*the extension in L of the sum of any family of* μ-(α-) *ideals of N contains* (*equals*) *the sum of their extensions; while the extension of their product is contained in the product of the extensions; when the family of ideals is finite, the extension of the product equals the product of their extensions.*"

Next we have an important relation between an ideal of N and its extension.

(2·5) "*Any ideal J of N is the intersection with N of its extension in L.*" For, let J′ be the intersection with N of the extension K of J. It is clear that $J \subset J'$. On the other hand, if c is in J′ then c is in N and in K, so that there is an element d of J such that $c < d$ ($c > d$). Since J is a μ-(α-) ideal of N, and d is in J, c is also in J which proves that $J' \subset J$. Thus $J' = J$ which proves (2·5).

From (2·5) and the definition of extension we infer that

(2·6) "*the extension of the ideal J of N is the least ideal of L intersecting N in J.*"

From (2·5) we deduce that, given two ideals J, J′ of N, $J \supset J'$ if, and only if, the extension of $J \supset$ the extension of J′; and so if two ideals have the same extension they are identical.

From the above remarks it follows that those μ-(α-) ideals of L which occur as extensions of the μ-(α-) ideals of N form an ordered set E_μ (E_α) isomorphic† to the lattice of μ-(α-) ideals of N. Hence E_μ, E_α are complete

† An isomorphism is a (1−1) correspondence which preserves order both ways. See MacNeille (1) (§ 5·6).

lattices with all sums distributive. From (2·4) we deduce that E_μ is a subsystem of L_μ relative to finite multiplication, while E_α is a subsystem of L_α relative to finite multiplication and unrestricted addition.

Finally we shall consider a result of which the dual is not true.

(2·7) "*the intersection with N of any α-ideal of L is an α-ideal of N.*" For, if *a, b* are in N and in the α-ideal K of L, then $a \cdot b$ is in N and in K and any element of $N > a$ is also in N and in K. Hence the result.

Since the ideal product of any family of α-ideals of N is their set-product it follows from (2·7) that,

(2·8) "*the intersection with N of the product of any family of α-ideals of L equals the product of their intersections.*"

From (2·5) and (2·7) it follows that an α-ideal of L is the extension of an α-ideal of N if, and only if, it is generated in L from the elements of N in it.

It may be proved easily that the extension of an ideal J of N is principal if, and only if, J is principal in N, and that the extension of the cut-complement of an ideal J of N is contained in the cut-complement of the extension of J.‡ These may be proved by the reader.

In the special case "*when N is a sub-lattice of L, an ideal of L is the extension of an ideal of N if, and only if it is the sum of a set of principal ideals generated by elements of N.*" (2·9)

For, if K is the extension of the μ-ideal J of N, then it is obviously equal to $\Sigma_{a \in J} P_\mu(a)$; while, if $K = \Sigma_{a \in S} P_\mu(a)$, where S is any set of elements of N, then K contains all finite sums in L (and so, in N) of the elements of S; hence, if J is the μ-ideal of N generated from the elements of S, K contains J and, as $K = \Sigma_{a \in S} P\mu(a)$, each element of K is $<$ an element of J. Therefore, by (2·1), K is the extension of the ideal J. This proves the result for μ-ideals, the dual is proved similarly. As an application of this result, we may note that

"*an ideal of L is the sum of simple ideals if, and only if, it is the extension of an ideal of S,*" (2·91) where S is the Boolean Algebra of simple elements of L.

§3 *Notation.*—L is a distributive lattice with 0, 1 in which every element has a product-complement and N is the set of normal elements of L. It is known for such a lattice, L, that N is a Boolean Algebra and a subsystem

‡ For definition of "cut-complement" see Vaidyanathaswamy (4).

of L relative to finite multiplication.¶ Hence we can have extensions in L of ideals of N. As usual, we denote the Boolean complement in N of an ideal A of N by $\bar{A}$.

We have now some further results in addition to those of §2. (2·6) gives one extreme value to the α-ideal of L having a given intersection with N. Now we get the other extreme value.

(3·1) "*the greatest α-ideal of L intersecting N in a given α-ideal J of N is the set K of elements c for which $c'' \in J$.*"

Firstly we see that K is an α-ideal of L. For, since J contains together with a'', b'' also $a''.b'' = (a \cdot b)''$ and $(a'' + c'')'' = (a + c)''$ where c is any element of L, K contains together with a, b also $a \cdot b$ and $a + c$, which proves that K is an α-ideal. Next we prove that the α-ideal of N, in which, by (2·7), an α-ideal P of L intersects N, consists of the elements c'', $c \in P$; for, since P is an α-ideal and $c < c''$, therefore, whenever $c \in P$, c'' is an element of N in P; conversely, an element d of N in P is of the form c'', $c \in P$, since $d = d''$.

From this result it follows that K intersects N in J and that, if an α-ideal P intersects N in J, then P is contained in K. This completes the proof of (3·1). This greatest α-ideal K intersecting N in J we shall call "*the complete original of J.*"‖

From (2·4) and (3·1) it follows also that the ideals lying between the extension of J and the complete original of J comprise all the α-ideals of L intersecting N in J.

By using the distributivity of finite products and the result $(a \cdot b)'' = a'' \cdot b''$ we can deduce from (3·1)

(3·2) "*the intersection with N of the sum of any family of α-ideals of L is the sum of their intersections with N.*"

Next we obtain a condition for a μ-ideal of L to be the extension of a μ-ideal of N.

(3·3) "*A μ-ideal of L can be the extension of a μ-ideal of N if, and only if, it contains a'' whenever it contains a.*"

For, if K is the extension of the μ-ideal J of N, then any element a of K is $<$ an element $b = b''$ of J, by (2·1); hence $a'' < b'' = b$ so that a'' is in K also. Conversely, let the μ-ideal K contain a'' whenever it contains a. In the first

¶ The proof of this when L is the lattice of ideals of a Boolean Ring, as given by M. H. Stone can be adapted for this case also. See Stone (3) {Th. 29}.

‖ For it is the complete original in the lattice homomorphism from L to N determined by the correspondence $a \to a''$. For a μ-ideal J of N, the complete original is, obviously, the extension.

place, we see that, if P is any μ-ideal of L, the set, J, of elements a'', $a \epsilon P$ is a μ-ideal of N; for, since P contains together with a, b also $a+b$ and $a \cdot c$, where c is any element of L, J contains together with a'', b'' also $(a+b)'' = (a''+b'')''$ and $(a \cdot c)'' = a'' \cdot c'' = a'' \cdot c$ where c is any element of N. Hence J is a μ-ideal of N. If now J′ is the μ-ideal of N formed by the elements a'', $a \epsilon K$, it follows from the assumption about K, that K contains J′; also for each a of K there is a'' in J such that $a < a''$. Hence K is the extension of the μ-ideal J′ of N. This completes the proof of (3·3).

Finally, we have as an addition to (2·4)

(3·4) "*the extension of the product of any family of μ-ideals of N equals the product of their extensions.*"

For, by (2·4) the extension of the product is contained in the product of the extensions. Now, if c is in the product of the extensions, c is in each extension, so that each of the μ-ideals of N contains an element (of N) $> c$; hence, since c'' is the least element of $N > c$, each of the μ-ideals of N contains c'' so that c'' is in the product of these ideals. Therefore, as $c < c''$, c is in the extension of the product of the ideals of N. This completes the proof of (3·4).

From (3·4) it follows that the extension of a comprincipal μ-ideal of N is a comprincipal μ-ideal of L*.

§4. *Notation.*—As in §3, L is a distributive lattice with 0, 1 admitting product complements and N is the Boolean Algebra of normal elements of L. $\bar{A}$ denotes the Boolean complement in N of the ideal A of N. {The Boolean complement of a μ-ideal is an α-ideal and *vice versa*; $\bar{\bar{A}} = A$; and $\overline{\Sigma_\gamma A_\gamma} = \Sigma_\gamma \overline{A_\gamma}$, $\overline{\Pi_\gamma A_\gamma} = \Pi_\gamma \overline{A_\gamma}$ where $\{A_\gamma\}$ is any family of μ-(α-) ideals of N†} The Boolean complement of an element in N in the same as its product-complement in L.

The elementwise-complement of an ideal of L

This is the generalisation of the Boolean complement of an ideal, to a lattice admitting product-complements.

"*The elementwise-complement*" of an ideal of L is defined to be the set of product-complements of the elements of the ideal.

Since the sum and product in N of the elements a', b' are respectively $(a'+b')'' = (a \cdot b)'$ and $a' \cdot b' = (a+b)'$, it follows easily that "*the elementwise-complement of a μ-ideal of L is an α-ideal of N*" *and vice versa*; and also that

* For the definition of "Comprincipal ideals" see Vaidyanathaswamy (4).

† For proofs see Pankajam (5) {Th. 18.}.

(4·1) " *the elementwise-complement of the sum (product) of any family (any finite family) of* μ- *or* α-*ideals of L is the sum (product) of the elementwise complements of the individual ideals.*"

I shall now express the elementwise-complement in terms of the Boolean complement in N and also find the greatest ideal of L with a given elementwise-complement. The results for μ-ideals and α-ideals are not of the same form. For the α-ideal the result is

(4·2) " *the elementwise complement of the* α-*ideal K of L is the Boolean complement in N of the intersection,* K_N, *of K with N.*"

For, K_N is an α-ideal of N, by (2·7), and consists of the elements a'', $a \epsilon K$ [as shown in the proof of (3·1)]. Hence, since $a' = a'''$, the Boolean complement of K_N, consisting of the elements a', $a \epsilon K$, is the elementwise complement of K.

Since $\underset{\nu}{\Pi} A_\nu = \overline{\Pi \bar{A}_\nu}$ when the set $\{A_\nu\}$ is a family of α-ideals of N, it follows by (2·8) and (4·2) that (4·3) " *the elementwise-complement of the product of any family of* α-*ideals of L is the product of their elementwise-complements.*"

A corresponding result for μ-ideals is not true.

From (4·2), (2·6) and (3·1) we deduce that (4·4) " *the greatest and least* α-*ideals of L having a given* μ-*ideal J of N as elementwise-complement are respectively the complete original of* $\bar{J}$ *and the extension of J.*"

The result corresponding to (4·2) for a μ-ideal is (4·5) " *the elementwise-complement of a* μ-*ideal K of L is the Boolean complement of the least* μ-*ideal of N whose extension contains K.*"

For, the set J of elements a'', $a \epsilon K$ is a μ-ideal of *N* [as shown in the proof of (3·3)], and the extension of J contains K, since $a < a''$. If the extension Q of any μ-ideal P of N contains K, then, by (3·3), Q contains J also; hence, since $J \subset N$ and, by (2·5), P is the intersection with N of Q, $J \subset P$. Thus J is the least μ-ideal of N whose extension contains K, and its Boolean complement, consisting of the elements a', $a \epsilon K$, is the elementwise-complement of K. This proves (4·5).

From (4·5) we can deduce that

(4·6) " *the greatest* μ-*ideal of L which has a given* α-*ideal J of N as elementwise-complement is the extension, K, of* $\bar{J}^*$ ".

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* Since the extension of $\bar{J}$ is its complete original, this result is the dual of the corresponding result in (4·4).

For, since $\bar{J}$ is the least μ-ideal of N whose extension contains K, $\bar{\bar{J}} = J$ is the elementwise-complement of K, by (4·5). And if the μ-ideal P of L has J as its elementwise-complement, then by (4·5), as $J = \bar{K}$ implies $K = \bar{J}$, $\bar{J}$ is the least μ-ideal of N whose elementwise-complement contains P, so that K contains P. This proves the result.

The product-complement of a μ-ideal can be related to the elementwise complement thus:

(4·7) " *the product-complement of the μ-ideal K of L is the extension of the cut-complement in N of the elementwise-complement of K.*"

For the product-complement of the μ-ideal K of L is $K' = \prod_{a \epsilon K} P_\mu' (a) = \prod_{a \epsilon K} P_\mu (a')$; and $P_\mu (a')$ is the extension of the principal ideal $P_{\mu N} (a')$ of N generated from the element a' of N. Hence, by (3·4), K′ is the extension of the product in N of the ideals $P_{\mu N} (a')$, $a \epsilon K$, of N; but the cut-complement in N of the elementwise-complement of K is the product in N of the ideals $P_{\mu N} (a')$, $a \epsilon K$. Hence, K′ is the extension of the cut complement in N of the elementwise-complement of K.

From (4·7) we see, firstly, that every normal μ-ideal of L is also comprincipal as it is the extension of a comprincipal μ-ideal of N. Next, since, by (4·6), there is always a μ-ideal which has a given α-ideal, J, of N as elementwise-complement, it follows, from (4·7) that the extension of the cut-complement of the arbitrary α-ideal, J, of N is the product-complement of a μ-ideal of L, and so is a normal μ-ideal.

Therefore, we have the result

(4·8) " *a μ-ideal of L is normal if, and only if, it is the extension of a comprincipal μ-ideal of N.*"

Since the comprincipal ideals are identical with the normal ideals in the Boolean Algebra N,* we can replace " *comprincipal* " by " *normal* " in (4·8).

Using (4·7) I next prove that

(4·9) " *the extension of the product-complement in N of a μ-ideal of N is the product-complement in L of its extension.*"

For, let J be a μ-ideal of N, J′ its product-complement in N, and K the extension of J. The product-complement K′ of K is the extension of the cut-complement in N of the elementwise-complement of K; but, by (4·5), since J is the least ideal of N whose extension contains K, the elementwise complement of

* See Pankajam (5) {Th. 25.}

K is J. Hence K′ is the extension of the cut-complement in N of the Boolean complement of J, that is, the extension of J′, since J′ is the cut-complement of J.*

From (4·8), we infer that the set N_μ of normal μ-ideals of L consists of the elements of E_μ which correspond to the normal (or comprincipal) μ-ideals of N in the isomorphism from the μ-ideals of N to the elements of E_μ. From (3·4) and (4·9), we see that $E\mu$ is a subsystem of L_μ relative to unrestricted products and product complements.

But we cannot dually assert that the class N_α of normal α-ideals are the elements of E_α corresponding to the normal (or comprincipal) α-ideals of N.

§5 *Notation.*—L is a general distributive lattice with 0, 1. As in the introduction, L_μ, L_α are the complete lattices consisting of the μ- and α-ideals respectively of L; and N_μ, N_α are the Boolean Algebras of normal elements of L_μ, L_α. We denote the sub-lattices of L_μ, L_α consisting of the principal μ- and α-ideals of L respectively by P_μ, P_α and the sets of product-complements of the elements of these in L_μ, L_α by Q_μ, Q_α. Q_μ, Q_α are sub-lattices of N_μ, N_α, as P_μ, P_α, are sub-lattices of L_μ, L_α. P_μ is directly isomorphic to L, and P_α is inversely isomorphic to L.†

The sector-ideal of L_μ or L_α generated by an ideal of L.

Given an α-ideal K_α (μ-ideal K_μ) of L, the set $K_{\alpha\alpha}$ ($K_{\mu\alpha}$) of elements of L_μ (L_α) which have a non-null intersection with K_α (K_μ) form an α-ideal of L_μ (L_α), which is called "*the sector ideal*" of L_μ (L_α) generated by K_α (K_μ).

$K_{\alpha\alpha}$ is easily seen to be an α-ideal of L_μ; for if the μ-ideals C, D of L intersect K_α in *c*, *d* respectively, C. D intersects K_α in *c*. *d*, and any μ-ideal containing C also interesects K_α in *c*. Similarly $K_{\mu\alpha}$ may be shown to be an α-ideal of L_α.

The sector-ideal may also be exhibited as the extension of an α-ideal of P_μ or P_α. For, the set $\overline{K_{\alpha\alpha}}$ ($K_{\mu\alpha}$) of elements of P_μ or P_α having a non-null intersection with K_α (K_μ) is easily seen to be an α-ideal of P_μ, (P_α) contained in $K_{\alpha\alpha}$ ($K_{\mu\alpha}$) and each element of $K_{\alpha\alpha}$ ($K_{\mu\alpha}$) is seen to contain an element of $\overline{K_{\alpha\alpha}}$ ($\overline{K_{\alpha\mu}}$). Hence, by (2·1), $K_{\alpha\alpha}$ ($K_{\mu\alpha}$) is the extension in $L\mu$ (L_α) of the α-ideal $\overline{K_{\alpha\alpha}}$ ($\overline{K_{\alpha\mu}}$) of the sub-lattice P_μ (P_α). From this and the results of § 2 we can deduce other results relating to sector-ideals. For instance, since P_μ, P_α are respectively, directly and inversely isomorphic to L, we deduce from (2·4) that

* See Pankajam (5) {Th. 24} This is the same as result 4·7 for the Boolean Algebra N.

† See Stone (2).

(5·1) " *the sector-ideal generated by the sum (product) of any family of μ- or α-ideals of L equals (is contained in) the sum (product) of the sector-ideals generated by the individual ideals; while if the family is finite, the sector-ideal generated by the product equals the product of the sector-ideals generated by the individual ideals.*"

Note.—It is seen that the cut-complement in L_μ (L_α) of the sector-ideal $K_{\alpha\alpha}$ ($K_{\mu\alpha}$) is the principal μ-ideal of L_μ (L_α) generated by the cut-complement in L of K_α (K_μ).

§ 6 *Notation.*—L is a Boolean Algebra, and so it is identical with the sets N and S of normal and simple elements respectively of L. Also, since the Boolean complement d' of an element d is also the product and sum-complement of d, the Boolean complement of an ideal of L is now also its elementwise-complement.

The last-residue-class in the Boolean Algebra L.

Since S = L, it follows that the intersection of an ideal of L with S is the ideal itself and the only ideal of L intesecting S in a given ideal of S is that ideal of S.

Hence, by (1·2), it follows that

(6·1) " the *last-residue-class of an ideal of L is the Boolean complement of the ideal*".

From (6·1) and the results $A = \overline{\bar{A}}$ and $A = \overline{B}$ if, and only if, $B = \bar{A}$, we deduce

(6·2) " *any ideal K of L is the last-residue-class of just one ideal of L, namely,* $\overline{K}$ ",

and

(6·2) " *every ideal of L is equal to the last-residue-class of its last-residue-class.*

The results (6·1), (6·2) and (6·3) give the solutions of the problems (P. 1), (P. 2) and (P. 3) respectively for the Boolean Algebra L.

§ 7 *Notation.*—L is a distributive lattice with 0, 1 in which every element has a product-complement and N is the Boolean Algebra of normal elements of L. As usual the Boolean complement in N of an ideal A of N is denoted by $\bar{A}$. In this section I obtain the solution of (P. 1) for an α-ideal of L, and of (P. 2) for a μ-ideal of L.

The last-residue-class of an α-ideal of L

The element c of L is in the last-residue-class of the α-ideal K of L if, and only if, an element d exists in K such that $c \cdot d = 0$ or, equivalently, $c < d'$; but the condition for c to be in the extension of the elementwise-complement of K is also that an element d should exist in K such that $c < d'$. Hence, it follows that

(7·1) " *the last-residue-class of an α-ideal K of L is the extension of its elementwise complement.*"

Using the results (2·4), (3·4), (4·1) and (4·3) we may deduce from (7·1) that

(7·2) " *the last-residue-class of the sum* (*product*) *of any family of α-ideals of L contains* (*equals*) *the sum* (*product*) *of their last-residue-classes* ".

From (7·1), we see that the last-residue-class of an α-ideal of L is the extension of a μ-ideal of N, namely, the elementwise-complement of the α-ideal. Conversely, since, by (4·4), there is always an α-ideal of L which has any given μ-ideal J of N as elementwise-complement, the extension of the arbitrary μ-ideal J of N is the last-residue-class of some α-ideal of L. Hence we deduce that a μ-ideal of L is the last-residue-class of some α-ideal if, and only if, it is the extension of a μ-ideal of N, that is, is in E_μ. Hence, by (3·3),

(7·3) " *a μ-ideal of L is the last-residue class of an α-ideal if, and only if, it contains a'' whenever it contains a* ".

(7·1) gives the solution of (P. 1) for an α-ideal, and (7·3) gives the solution of (P. 2) for a μ-ideal.

Since by (2·7) an ideal of L cannot be the extension of more than one distinct ideal of N, we can deduce from (7·1), by using (4·4), that

(7·4) " *the greatest and least α-ideals of L having the extension of a μ-ideal J of N as their last-residue-class are respectively the complete original of J and the extension of* $\bar{J}$."

§ 8 *Notation.*—L, L_μ, L_α, N_μ, N_α, P_μ, P_α, Q_μ, Q_α have the same significance as in § 5; also, as in §5, the set of elements of L_μ, and P_μ, [L_α and P_α] having a non-null intersection with a given α-ideal K_α [μ-ideal K_μ] of L are denoted respectively by $K_{\alpha\alpha}$ and $\bar{K}_{\alpha\alpha}$ [$K_{\mu\alpha}$ and $\bar{K}_{\alpha\mu}$].

The last-residue-class in the general distributive lattice with units.

The following is the solution of (P. 1):

(8·1) "*the last-residue-class of the* α*-ideal* K_α (μ*-ideal* K_μ) *of L is the ideal sum of the elements in the extension in* L_μ (L_α) *of the elementwise-complement of the sector-ideal of* L_μ (L_α) *generated by* K_α (K_μ)."

Firstly the last-residue-class of K_α is $\sum_{a \in K_\alpha} P_\mu'(a)$. For, since the product of any element of $P_\mu'(a)$ with a is 0, therefore, $P_\mu'(a)$, $a \in K_\alpha$ and, hence, $\sum_{a \in K_\alpha} P_\mu'(a)$ is contained in the last-residue-class of K_α. Conversely, if c is in the last-residue-class of K_α, there is an element d in K_α such that $c \cdot d = 0$; hence $c \in P_\mu'(d)$, $d \in K_\alpha$ which shows that the last-residue-class of K_α is also contained in, and so is equal to, $\sum_{a \in K_\alpha} P_\mu'(a)$. Next, the set F of elements of Q_μ of the form $P_\mu'(a)$, $a \in K_\alpha$ is a μ-ideal of Q_μ; for, since K_α contains together with a, b also $a \cdot b$ and $a+c$, where c is any element of L, F contains together with $P_\mu'(a)$, $P_\mu'(b)$ also $P_\mu'(a \cdot b) = [P_\mu'(a) + P_\mu'(b)]''$ and $P_\mu'(a+c) = P_\mu'(a)$. $P_\mu'(c)$ where $P_\mu'(c)$ is any element of Q_μ. Hence F is a μ-ideal of Q_μ and the last-residue-class of K_α is $\sum_{c_\gamma \in F} C^\gamma$. F is the set of product complements in L_μ of the elements of $\overline{K_{\alpha\alpha}}$. Hence, since $K_{\alpha\alpha}$ is the extension of $\overline{K_{\alpha\alpha}}$, the elementwise-complement of $K_{\alpha\alpha}$ is easily seen to be the extension in N_μ of the μ-ideal F of Q_μ. Hence, the sum in L_μ of the elements in the extension in L_μ of the elementwise-complement of $K_{\alpha\alpha}$, is, by (2·3) and (2·2), equal to $\sum_{c_\gamma \in F} C^\gamma$ = the last-residue-class of K_α. This completes the proof of the proposition for an α-ideal; the dual is similarly proved.

The solution of (P. 2) for the general distributive lattice is now given by (8·2) "*a* μ-(α-) *ideal of L can be the last-residue-class of an ideal of L if, and only if, it can be expressed as the sum of the elements in the extension in* L_μ (L_α) *of a* μ*-ideal of* Q_μ (Q_α)".

This, by (2·2), is the same as saying that the ideal should be expressible as the sum in L_μ (L_α) of the elements of a μ-ideal of Q_μ (Q_α). From the proof of (8·1) the condition is seen to be necessary for a μ-ideal to be the last-residue-class of an α-ideal. If, conversely, the μ-ideal $K_\mu = \sum_{c\gamma \in F} C^\gamma$, where F is a μ-ideal of Q_μ, then the set P of elements c for which $P_\mu'(c) \in F$ form an α-ideal of L. For, since F contains together with $P_\mu'(a)$, $P_\mu'(b)$ also $[P_\mu'(a) + P_\mu'(b)]'' = P_\mu'(a \cdot b)$ and $P_\mu'(a) \cdot P_\mu'(c) = P_\mu'(a+c)$, where

c is any element of L, P contains together with a, b also $a \cdot b$ and $a + c$; hence P is an α-ideal of L. And by the proof of $(8 \cdot 1)$, the last-residue-class of P is seen to be $\sum_{c\gamma \in F} C_r = K$; this proves that the condition is also sufficient for a μ-ideal to be the last-residue-class of an α-ideal. The dual result is proved similarly.

Finally, analogous to $(7 \cdot 4)$ we can note that for the ideal $K = P_\mu(0)$ $[= P_\alpha(1)]$ the least and greatest ideals of L having K as last-residue-class exist and are respectively $P_\alpha(1)$ $[P_\mu(0)]$ and the set K_0 $[K_1]$ of elements of L which have 0 (1) as product- (sum-) complement.*

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* K_0 is an α-ideal; for $c' = 0$ if, and only if, $c \cdot x = 0$ implies $x = 0$ for all x of L; hence, if $c' = 0$, $d' = 0$ and $e > c$, then $c \cdot d \cdot x = 0$ implies $d \cdot x = 0$ which implies $x = 0'$; and $e \cdot x = 0$ implies $c \cdot x = c \cdot e \cdot x = 0$ which implies $x = 0$. Hence $(c \cdot d)' = 0$ and $e = 0$, so that K_0 contains together with c, d also c, d and e. Similarly K_1 is shown to be α μ-ideal.

ERRATA

Page No.	Line No.	B=from the bottom T=from the top	*For*	*Read*
178	3	B	a is in S	a is in S ;
179	12	B	$a + b > a \oplus b$	$a \oplus b > a + b$
„	2	B	$c > c_1 \oplus \cdots \oplus c_n$	$c < c_1 + \cdots + c_n$
„	1	B	$> c_1 + \cdots + c_n = d$ ($c < c_1 \cdots c_n = d$).	$< c_1 \oplus \cdots \oplus c_n = d$ ($c > c_1 \cdots c_n = d$).
184	14	T	Since $\Pi_\nu A_\nu = \overline{\Pi}_\nu \overline{A}_\nu$ when the set $\{A_\nu\}$	Since $\overline{\Pi}_\nu A_\nu = \Pi_\nu \overline{A}_\nu$ when the set $\{A_\nu\}$ . . . .
185	4	T	whose elementwise-complement contains P	whose extension contains P
186	8	B	$\overline{K}_{\alpha\alpha}$ ($K_{\mu\alpha}$) of elements of P_μ or P_α	$\overline{K}_{\alpha\alpha}$ ($\overline{K}_{\mu\alpha}$) of elements of P_μ (P_α)
„	5 & 4	B	$\overline{K}_{\alpha\alpha}$ ($\overline{K}_{\alpha\mu}$)	$\overline{K}_{\alpha\alpha}$ ($\overline{K}_{\mu\alpha}$)
187	11	T	is also the product and sum-	is also the product-and sum-
188	9	B	Since by (2·7)	Since by (2·6)
„	1	B	[$K_{\mu\alpha}$ and $\overline{K}_{\alpha\mu}$].	[$K_{\mu\alpha}$ and $\overline{K}_{\mu\alpha}$].
189	19, 14 & 4	B	$\Sigma'_{C_r \epsilon F} C^r$	$\Sigma'_{C_r \epsilon F} C_r$
190	3	B	$x = 0'$;	$x = 0$;
(*Footnote*)	2	B	$e = 0$,	$e' = 0$,
„	1	B	with c, d also c, d and e.	with c, d also $c \cdot d$ and e.

ON TEN ASSOCIATED POINTS IN [4]

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Any m points $P_1, P_2, \cdots P_m$ in $[n]$ are said to be associated, when every quadric through any $m-1$ of them passes through the remaining point. A necessary and sufficient condition for this, is the existence of an identity of the form

$$\sum_{r=1}^{m} \lambda_r P_r^2 \equiv 0.$$

F. Bath has proved the following theorem*:—*Given* 10 *associated points in* [4] *which do not lie upon a rational quartic curve, the rational quartic through any seven of them has the plane of the remaining three as a trisecant plane; also the three points and the three intersections with the quartic lie on a conic.* The object of this note is to give an alternative proof of the above theorem by making use of the theory of the inpolar quadric of a rational norm curve.

A quadric envelope Q in $[n]$ is said to be inpolar to a rational norm curve R^n, if it is a polar to all quadrics containing R^n. If an inpolar quadric Q is degenerate and of rank $(k+1)$ where $k < n$, its singular region is a secant $[k]$ of R^n (*i.e.*) cutting R^n at $k+1$ points $A_1, A_2, \cdots A_{k+1}$.† Further the equation of Q can be expressed in the form

$$\sum_{r=1}^{1+k} \mu_r A_r^2 = 0.$$

In particular A_r^2 is a degenerate inpolar quadric of rank one.

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* *Journal London Math. Soc.*, 1938, **13**, 198.

† With every inpolar quadric Q of R^n is associated the polar form $a_x^n a_y^n$ of a binary form a_x^{2n}. If Q is of rank $(k+1)$, a_x^{2n} can be expressed as the sum of $(k+1)$ perfect $2n$th powers and conversely. The result above, follows from this.

See Vaidyanathaswamy, "On polar forms and closed forms," *Journal Indian Math. Soc.*, 1929, **18**, 168–76.

Let us take 10 associated points P_1, P_2, , P_{10} in [4]. Then there is identity of the form $\sum_1^{10} \lambda_r P_r^2 \equiv 0$. Hence

$$Q \equiv (\lambda_1 P_1^2 + \lambda_2^2 P_2^2 + \lambda_3 P_3^2) = -(\lambda_4 P_4^2 + \cdots \lambda_{10} P_{10}^2).$$

If we take the unique rational quartic curve R^4 through the seven points P_4, P_5, , P_{10}, then P_4^2, P_5^2, $\cdots$ P_{10}^2 are inpolar quadrics of R^4 and hence Q is also an inpolar quadric. But $Q \equiv \lambda_1 P_1^2 + \lambda_2 P_2^2 + \lambda_3 P_3^2$. Hence it is of rank 3, and its singular plane is $P_1 P_2 P_3$. Hence $P_1 P_2 P_3$ must be a secant plane of R^4 cutting R^4 at three points, say $A_1 A_2 A_3$.

Then $$Q \equiv \mu_1 A_1^2 + \mu_2 A_2^2 + \mu_3 A_3^2.$$

Therefore $$\lambda_1 P_1^2 + \lambda_2 P_2^2 + \lambda_3 P_3^2 - \mu_1 A_1^2 - \mu_2 A_2^2 - \mu_3 A_3^2 \equiv 0.$$

Since it is given that P_1 P_2 P_3 do not lie on R^4 they are different from A_1 A_2 A_3. The six points, in virtue of the above identity, form an associated set and hence lie on a conic.

The method of proof can be easily applied to have the generalisation relating to a set of $(2n+2)$ associated points in $[n]$, given by Bath at the end of his paper.

VISCOUS SOLUTIONS OBTAINED BY SUPERPOSITION OF EFFECTS

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When a solid moves slowly through a viscous liquid, so that the inertia terms can be neglected in the equations of motion, the solution of the corresponding problem may be obtained by the method of superposition of two solutions. One of these is the irrotational solution obtained by assuming the solid to be moving through a non-viscous liquid with a particular velocity, and the other is that due to a concentrated force applied in the direction of motion of the solid in an infinite viscous liquid. As is to be expected, the concentrated force in each case is the drag suffered by the solid. We propose to illustrate this method by discussing the cases of a sphere and a circular cylinder.

Motion of a Sphere

For a sphere of radius a moving with a velocity U in the direction of the x-axis the component velocities for the irrotational solution are given by

$$u_1 = -\frac{1}{2}\,\mathrm{U}\left(\frac{a}{r}\right)^3 + \frac{3}{2}\,\mathrm{U}\,\frac{x^2}{a^2}\left(\frac{a}{r}\right)^5, \tag{1·1}$$

$$v_1 = \frac{3}{2}\,\mathrm{U}\,\frac{xy}{a^2}\left(\frac{a}{r}\right)^5, \tag{1·2}$$

$$w_1 = \frac{3}{2}\,\mathrm{U}\,\frac{xz}{a^2}\left(\frac{a}{r}\right)^5. \tag{1·3}$$

We also know that for a force P acting at the origin along the x-axis in an infinite viscous liquid the component velocities are given by[1]

$$u_2 = \frac{\mathrm{P}}{8\pi\mu}\left(\frac{x^2}{r^3} + \frac{1}{r}\right), \tag{2·1}$$

$$v_2 = \frac{\mathrm{P}}{8\pi\mu}\cdot\frac{xy}{r^3}, \tag{2·2}$$

$$w_2 = \frac{\mathrm{P}}{8\pi\mu}\cdot\frac{xz}{r^3}, \tag{2·3}$$

μ being the coefficient of viscosity.

Let

$$u = Au_1 + u_2, \tag{3·1}$$

$$v = Av_1 + v_2, \tag{3·2}$$

$$w = Aw_1 + w_2, \tag{3·3}$$

where A is a constant to be determined from the boundary conditions. If u, v, w are to give the required solution, we should have $u = U$, $v = 0$, $w = 0$ over $r = a$. These conditions give $A = -\frac{1}{2}$, $P = 6\mu\pi a\, U$. P is obviously the value of the drag given by Stokes's solution. We also see that the velocity of the solid in the irrotational motion is $-\frac{1}{2}U$.

Motion of a Circular Cylinder

The corresponding results for a circular cylinder are given below.

$$u_1 = -\frac{Ua^2}{r^2} + \frac{2\,Ua^2x^2}{r^4}, \tag{4·1}$$

$$v_1 = \frac{2\,Ua^2xy}{r^4}, \tag{4·2}$$

$$u_2 = -\frac{P}{4\pi\mu}\left(\log r - \frac{x^2}{r^2}\right), \tag{6·1}$$

$$v_2 = \frac{Pxy}{4\pi\mu r^2}. \tag{6·2}$$

The solution given by (6) is defective as it makes the velocity logarithmically infinite at infinity.[1] Putting

$$u = Au_1 + u_2, \tag{7·1}$$

$$v = Av_1 + v_2, \tag{7·2}$$

we find

$$A = \frac{1}{2\log a - 1}, \tag{8·1}$$

$$P = \frac{4\pi\mu U}{\frac{1}{2} - \log a}. \tag{8·2}$$

This solution has been obtained by Berry and Swain.[2] The velocity in the irrotational motion is $-U/(1 - 2\log a)$, while the drag suffered

[1] Lamb, *Hydrodynamics*, 5th ed. (1930), pp. 579–81.

[2] Berry and Swain, *Proc. Roy. Soc.* (A), 1923, **102**, 770; also Seth, *Phil. Mag.*, 1939, ser. 7, **27**, 218.

by the cylinder is given by (8·2). As has been already pointed out, the solution is defective at infinity.

The values of the component velocities given by (2) and (6) are the displacements produced in an infinite elastic body by applying a force at the origin in the direction of the x-axis.[3] This analogy suggests the following known results.

(i) The solutions given by (3) and (7) hold good only for small values of the deformation velocities.

(ii) (3) and (7) give sufficiently correct results near the boundary of the body. Near the surface of the sphere Stokes's solution is known to give a better approximation than the one given by Oseen.[4]

[3] Love, *Theory of Elasticity*, 4th. ed. (1927), **185, 209.**

[4] Lamb, *Hydrodynamics*, 5th. ed. 1930, p. 579.

MAGNETIC STUDY OF THE REACTION $AsBr_3 + Br_2 \rightleftharpoons AsBr_5$

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1. Introduction

In the course of some experiments on the kinetics of the olefin-bromine reaction by Venkataraman (1941), it was found that arsenic tribromide appeared to exert a retarding influence. A fall in the concentration of "available" bromine indicated the combination of some of the bromine with arsenic tribromide in accordance with an equilibrium of the type $AsBr_3 + Br_2 \rightleftharpoons AsBr_5$.

No pentabromide of arsenic is described in literature (Mellor, 1929) but the observations of Venkataraman (1941) seem to get a natural explanation if a compound of this type is assumed to be formed between arsenic tribromide and bromine. It was believed that a magnetic study of the problem might throw some useful light on the subject.

The law of additivity of magnetic susceptibility has been investigated by a large number of workers, and shown to be generally true. Small changes have however been discovered.

Rao and Sriraman (1937) undertook a careful examination of the diamagnetic susceptibility of some complex ions. They have shown that departures from the additivity law may be observed when some salts are dissolved in water.

The percentage changes in these cases appear to be independent of concentration. These have been attributed to (*a*) interaction between the ions and water molecules, (*b*) de-polymerisation of water, (*c*) release of constraints within the molecules due to the breakage in the ions, and (*d*) change of valency of any of the ions when the salt is dissolved. The first two causes do not produce more than one percent change from the additive law. The other two causes give rise to much larger changes. In fact Subrahmanyam (1936) obtained as much as 22% increase on dissolving cadmium iodide in water. As an example of the change of susceptibility due to change of valency when a salt is dissolved in water, the case of selenites may be cited.

In the case of these salts, the diamagnetic susceptibility was found by Rao and Sriraman (1937) to increase on solution in water. This result supports the inference of Venkateswaran (1936) from Raman effect investigations that in the solid selenious acid, selenium is hexavalent and in aqueous solutions it becomes tetravalent.

Strong association or chemical action between the two components of a binary mixture might lead to relatively large changes from the law of additivity. It was felt that a study of the magnetic susceptibilities of mixtures of arsenic tribromide and bromine in the presence of acetic acid might lead to some useful information which might throw light on the reduction of the "available" bromine in investigations on chemical kinetics by Venkataraman (1941).

2. Experiment

(*a*) *Purification of liquids:*

(*i*) *Acetic acid.*—The purification of this acid was carried out by the method of Orton and Bradfield (1927). The purified specimen had a melting point of 16·6° C. indicating that the acid was 100% pure.

(*ii*) *Bromine.*—Bromine was purified by the method of Anantakrishnan and Ingold (1935). The purified bromine melted at $-7{\cdot}3°$ C.

(*iii*) *Arsenic tribromide.*—The Kahlbaum sample was distilled first under low pressure rejecting large head and tail fractions. It was further purified by solidification by immersing in ice water, and rejecting the first melt. The operation was repeated until a sample of constant melting point (31° C.) was obtained.

(*b*) *Preparation of mixture:*

Mixtures of arsenic tribromide and acetic acid and of bromine and acetic acid were prepared by weighing a suitable quantity of the bromide or bromine and adding enough acetic acid to make up a suitable volume which would give the concentration appropriately as so many mols per litre. In this manner solutions of arsenic tribromide in acetic acid were prepared to have the concentrations of 2M, 4M/3, M, 2M/3, M/2 and M/3 respectively per litre. Bromine solutions in acetic acid were prepared to have the same concentrations in mols per litre.

Equal volumes of bromine-acetic acid and arsenic tribromide-acetic acid solutions having equal concentration were then mixed together. If, for example, equal volumes of the 2M mixtures are mixed together, the concentration of arsenic tribromide or bromine in the mixture would become M per litre. The concentrations of the six mixtures thus prepared were

M, 2M/3, M/2, M/3, M/4 and M/6 per litre of arsenic tribromide and of bromine.

These concentrations will hold good only if there is no change of density when the mixtures are effected. From the following pages, it will be seen that there is a small change of density in the case of each mixture. Hence the above concentrations are only approximate.

(*c*) *Determination of specific susceptibility :*

The Gouy method was adopted for determining the specific susceptibility of the mixtures.

The standard substance used was water, whose diamagnetic specific susceptibility was assumed to be 0·720.*

(*d*) *Measurement of relative density :*

The relative density here measured is the ratio of the density of the liquid at 30° C. to the density of water at the same temperature. This relative density $\rho^{s}_{30}/\rho^{w}_{30}$ was determined by weighing equal volumes of the solution and water.

In the following measurements, the values of the relative densities of the liquids are given in terms of the density of water at 30° C.

3. Results

(*a*) *Pure liquids :*

The results obtained with bromine are given below.—

TABLE I

Bromine

Authors	Specific susceptibility	Relative density
I. C. T.	0·39	3·084
Honda	0·375	..
Owen (1912)	0·403	..
Rao and Govindarajan (1942) ..	0·346	3·074
Author	0·364	3·080

The above table shows that the value of the specific susceptibilities obtained in the present investigation is in close agreement with the results

* All susceptibility values in this paper are, unless otherwise stated, diamagnetic and are expressed in 10^{-6} unit.

of Honda (1910) and Rao and Govindarajan (1942). The value of Owen (1912) appears to be very high. The density values shown in column 3 of the table are in close agreement.

The specific susceptibility of acetic acid was found to be 0·529, which agrees well with the values of other investigators (*e.g.* I.C.T. 0·526).

Arsenic tribromide.—Arsenic tribromide appears to melt at 31° C. (Mellor, 1929, p. 248). Its relative density at the melting point according to Jager (Mellor, 1929, p. 248) is 3·381. In the present investigation this value is found to be 3·383 which agrees remarkably well with the above result.

The specific susceptibility of arsenic tribromide does not seem to have been studied before. Its value is found here to be 0·308. Taking the molecular weight of arsenic tribromide to be 314·7, the molecular magnetic susceptibility works to 96·9.

(*b*) *Arsenic tribromide in acetic acid :*

The results obtained with six concentrations of arsenic tribromide in acetic acid are given in Table II below.

TABLE II

$AsBr_3$ in CH_3COOH

Solution No.	Conc. of $AsBr_3$ in mols. per litre	% $AsBr_3$	% CH_3COOH	Relative density ρ	$\chi \times$ Cal.	$\chi \times$ Observed
	Pure As Br_3 ..	100	0	3·383	..	0·308
1	2M ..	41·82	58·18	1·505	0·437	0·432
2	4M/3 ..	31·00	69·00	1·355	0·460	0·459
3	M ..	24·66	75·34	1·276	0·475	0·476
4	2M/3 ..	17·48	82·52	1·200	0·490	0·488
5	M/2 ..	13·53	86·47	1·163	0·499	0·498
6	M/3 ..	9·29	90·71	1·129	0·508	0·510
	Pure CH_3COOH ..	0	100	1·042	..	0·529

An examination of the above table shows that the calculated and the observed values show considerable agreement. No systematic deviation of the observed values from those calculated on the basis of the law of additivity has been observed.

This conclusion indicates no change in the molecular property of either arsenic tribromide or acetic acid.

(*c*) *Bromine in acetic acid:*

TABLE III

Br_2 in CH_3COOH

Soln. No.	Conc. of Br_2 in mols. per litre.	% Br_2	% CH_3COOH	Relative density	χ Cal.	χ Obs.	χ Obs. $-\chi$ Cal.
	Pure Br_2 ..	100	0	3·080	..	0·364	..
1	2M ..	25·78	74·22	1·240	0·486	0·493	0·007
2	4M/3 ..	18·09	81·91	1·178	0·499	0·505	0·006
3	M ..	14·02	85·98	1·140	0·506	0·511	0·005
4	2M/3 ..	9·70	90·30	1·098	0·513	0·519	0·006
5	M/2 ..	7·40	92·60	1·079	0·517	0·521	0·004
6	M/3 ..	5·01	94·99	1·063	0·521	0·525	0·004
	Pure CH_3COOH	0	100	1·042	..	0·529	..

It may be seen from the above table that there is a small systematic deviation between the observed and calculated values of magnetic susceptibility. This difference however, is very small being about 1%. These results agree with the observations of Rao and Govindarajan (1942) who also found that the specific susceptibility of bromine in solution in acetic acid appears to be larger than additive values.

(*d*) *Arsenic tribromide and bromine in acetic acid:*

TABLE IV

$AsBr_3$ and Br_2 in CH_3COOH

Approxi. conc. of $AsBr_3$ & Br_2 in mols. per litre	% As Br_3	% Br_2	% CH_3COOH	ρ	χ Cal.	χ Obs.	$\chi_{Cal.} - \chi_{Ob.}$	$\frac{\chi_{Cal.} - \chi_{Ob.}}{Conc.}$
M	22·92	11·65	65·43	1·412	0·459	0·439	0·020	0·020
2M/3	16·58	8·41	75·01	1·296	0·479	0·464	0·015	0·022
M/2	13·04	6·62	80·34	1·228	0·489	0·477	0·012	0·024
M/3	9·14	4·66	86·20	1·172	0·501	0·492	0·009	0·027
M/4	7·00	3·57	89·43	1·133	0·507	0·500	0·007	0·028
M/6	4·79	2·42	92·79	1·105	0·514	0·509	0·005	0·030

A scrutiny of the above table shows that there is a systematic deviation between the calculated and observed values. The observed values are found to be systematically lower than the calculated values. The change of susceptibility per unit molar concentration shows a gradual increase with dilution. This probably indicates that the effects which we are studying are more prominent at smaller concentrations than at larger concentrations.

4. Discussion

We shall first consider the relative densities of the solutions. If a volume v c.c. of bromine solution in acetic acid of concentration 2M per litre and v c.c. of arsenic tribromide solution having the same molecular concentration per litre are mixed together, it is easy to see that the concentration of arsenic tribromide and bromine in the mixture is each only M in gm. molecules per litre. If no mutual interaction between the two solutions takes place, the density of the mixture will work to the mean of the densities of the two solutions. Table V given below indicates that when arsenic tribromide and bromine solutions are mixed together, the density of the mixture is less than the mean density of the solutions.

TABLE V

Densities

Conc. of Br_2 and $AsBr_3$ in mols. per litre	Rel. den. Br_2 in acid	Rel. den. $AsBr_3$ in acid	App. conc. of Br_2 and $AsBr_3$ in the mixture	Mean Rel. dens.	Observed rel. dens.	Difference
2M	1·240	1·505	M	1·372	1·412	0·040
4M/3	1·178	1·355	2M/3	1·267	1·296	0·029
M	1·140	1·276	M/2	1·208	1·228	0·020
2M/3	1·098	1·200	M/3	1·149	1·172	0·023
M/2	1·079	1·163	M/4	1·121	1·133	0·012
M/3	1·063	1·129	M/6	1·096	1·105	0·009

The above table indicates that when arsenic tribromide and bromine solutions are mixed together, a contraction in volume takes place, giving rise to a larger density for the mixture. The decrease of volume and the consequent increase in density are closely related with the concentrations of arsenic tribromide and bromine in the initial solutions. The larger the concentration of the constituents in the acid, the greater is the increase in density. This conclusion indicates a possible partial chemical combination or at least a close association between the molecules of arsenic tribromide and of bromine.

The above conclusion receives support from the changes of susceptibility observed in Table IV. The observed values of the susceptibility are uniformly lower than the calculated values. Before offering a discussion on this subject, the specific susceptibility of the mixture of the two solutions may be calculated in a different manner.

In the conclusion given in Table IV, the specific susceptibility of the final mixture is calculated from a knowledge of the percentage by weight

of arsenic tribromide, bromine and acetic acid, knowing the specific susceptibilities of each these chemicals.

Another method of calculating the specific susceptibilities of the mixtures in Table IV is to take the values from Tables II and III in the following manner. A litre of 2M arsenic tribromide solution has a mass of 1505 gm. The specific susceptibility observed for this solution is 0·432. We may write similarly from Table III that one litre of 2M bromine solution has a mass of 1240 gm. The specific susceptibility of this solution is 0·493. When the two solutions, each of one litre capacity are mixed together, there would be in all 2745 gm. The susceptibility per gm. of this mixture would work to

$$(1505 \times 0{\cdot}432 + 1240 \times 0{\cdot}493) \div 2745 \text{ or } 0{\cdot}459$$

Similar calculations have been made in the case of other concentrations. This procedure is probably more correct than the method adopted in Table IV since due account would have been taken of the small changes from additivity in the observed values of arsenic tribromide solutions given in Table II. These results are presented in Table VI.

TABLE VI

$AsBr_3$ and Br_2 in CH_3COOH

Conc. of $AsBr_3$ & Br_2 taken in mols. per litre (C)	Rel. den. of $AsBr_3$ soln.	x of $AsBr_3$ soln.	Rel. den. of Br_2 soln.	x of Br_2 soln.	x Cal.	x Ob.	$x_{Cal.} - x_{Obs.}$	$\frac{x_{Cal.} - x_{Obs.}}{C}$ in the mixture
2M	1·505	0·432	1·240	0·493	0·459	0·439	0·020	0·020
4M/3	1·355	0·459	1·178	0·505	0·480	0·464	0·016	0·024
M	1·276	0·476	1·140	0·511	0·493	0·477	0·016	0·032
2M/3	1·200	0·488	1·098	0·519	0·503	0·492	0·011	0·033
M/2	1·163	0·498	1·079	0·521	0·509	0·500	0·009	0·036
M/3	1·129	0·510	1·063	0·525	0·517	0·509	0·008	0·048

Possible combination of $AsBr_3$ *and* Br_2

A rough calculation may be made of the magnetic susceptibilities of the tribromide from our knowledge of the ionic susceptibilities of As^{+3} and Br^{-1}. Kido's (1933) values for the gram ionic susceptibilities of these ions are 10·1 and 34·7. This would give for $AsBr_3$ the value 114·2. But the experimentally deduced value of the molecular susceptibility of $AsBr_3$ is 96·9. Thus the paramagnetic component due to ionic deformation during the combination of As^{+3} and $3Br^{-1}$ is 17·3.

Assuming Kido's value of As^{+5} to be 1·9, the molecular susceptibility of $AsBr_5$ works to 172·37. In the absence of any definite value for the

deformation produced in this case, it is difficult to calculate the actual susceptibility per gram molecule of $AsBr_5$. An approximate method of evaluating the molecular susceptibility of $AsBr_5$ is to determine from our knowledge of the molecular susceptibility of $AsBr_3$, the ionic susceptibility of the deformed bromine ions. Since the molecular susceptibility of $AsBr_3$ is 96·9, and according to Kido, the ionic susceptibility of As^{+3} is 10·1, it follows that the ionic susceptibility of each deformed bromine ion is (96·9–10.1)÷3 or 28·9. It is reasonable to expect that the deformation of the bromine ions is much larger than the deformation of the arsenic ions. Assuming the same amount of deformation of the bromine ions in arsenic pentabromide, and Kido's value of 1·9 for As^{+5}, the molecular susceptibility of $AsBr_5$ works to $1 \cdot 9 + 5 \times 28 \cdot 9$ or 146·4.

On the other hand the sum of the molecular susceptibilities of $AsBr_3$ and Br_2 is $96 \cdot 9 + 79 \cdot 91 \times 2 \times 0 \cdot 364$ or 155·1. Thus, if one mol. of arsenic tribromide combines with one mol. of bromine to give rise to one mol. of arsenic pentabromide, the total molecular susceptibility would appear to fall from 155·1 to 146·4. Hence if arsenic tribromide and bromine in the medium of acetic acid combine together to form the pentabromide, there would apparently be a decrease of susceptibility which is obviously not less than about 6% and probably much greater.

It is also clear from the magnitudes of the quantities involved that not all the arsenic tribromide and bromine combine with each other to produce the pentabromide. An examination of Table VI shows that the departure from the additivity law when arsenic tribromide and bromine solutions are mixed together, is less than 4%.

It appears also likely that the combination between arsenic tribromide and bromine increases at greater dilutions.

That the changes from additivity could not be due to any changes in the molecular constitution of acetic acid is clear, since bromine solutions in acetic acid show comparatively small departure from the additive law and arsenic tribromide solutions do not show any deviation. Rao and Varadachari (1934) showed that heating acetic acid to about 100° does not produce any striking change in the susceptibility of the acid. This would indicate that a break down of any association that might exist in acetic acid at room temperature, does not lead to any change of susceptibility.

The conclusions of this investigation support the observations of Venkataraman (1941). In studying the kinetics of the olefin-bromine reaction, he found that control experiments with the tribromide of arsenic

indicated a fall in concentration of 'available' bromine. This diminution was found to be a function of concentration.

Possible association of $AsBr_3$ *and* Br_2 *:*

There is another possibility which may account both for the observed change of susceptibility in this investigation and the reduction in concentration of 'available' bromine observed by Venkataraman (1941). A strong association between arsenic tribromide and bromine might result in the deformation of the electron orbits and the consequent appearance of paramagnetism.

By association is implied the aggregation of single molecules into complexes containing two or more of the single molecules. The degree of association is the fraction of the single molecules which have formed aggregates. Such intermolecular action is to be explained by the stray electric forces associated with molecules because of the existence of dipoles. The forces exerted by these dipoles vary inversely as the cube of the distance. The bromine molecule Br_2 has a dipole moment of $0{\cdot}45 \times 10^{-18}$ (Smyth, 1931, p. 192). Although the dipole moment of arsenic tribromide does not seem to have been worked out, it seems clear that it should have a comparatively large value since according to the information given by Smyth, the halides of antimony show a large dipole moment. It is likely therefore that arsenic tribromide and bromine form strong complexes in the medium of acetic acid.

The arsenic-bromine bond : .

Much useful information is available regarding the nature of the chemical bond between the halogens and the elements of the fifth group (Pauling, 1939, pp. 210–18). Generally an element of the fifth group is attached by a single covalent bond to each of the attached halogen atoms. In the case of lighter elements, there is evidence from the work of Gregg, Hampson, Jenkins, Joans and Sutton (1937) that there is in addition a partial double-bond character of the bonds. They have shown that the inter-atomic distances are found to be slightly less than the sum of the ionic radii, whenever the double bond character was prominent. In the case of arsenic tribromide, the results now on record do not show any agreement. Whereas Gregg and others (1937) obtained no change in the inter-atomic distance, Hassel and Sandbo (1938) observed about 1·6% decrease of inter-atomic distance. Magnetic data obtained above relating to arsenic tribromide indicate that the latter workers are probably correct. In fact one would expect much greater decrease in the inter-atomic distance than 1·6%.

A careful investigation of the susceptibilities of the halides of the elements of the fifth group in relation to the nature of their chemical bond appears necessary. Work in this direction is being instituted in this laboratory.

I take this opportunity of thanking Dr. S. V. Anantakrishnan who suggested this problem, and Mr. R. Venkataraman, who helped me in the purification of the chemicals. My thanks are also due to Dr. S. Ramachandra Rao for his interest in this work.

Summary

In the course of some experiments on the kinetics of the olefin-bromine reaction, Venkataraman found that the available bromine showed a decrease in concentration in the presence of arsenic tribromide. He suggested a possible combination of arsenic tribromide with bromine to give the pentabromide of arsenic. In the present investigation, this problem is studied from the magnetic point of view. Solutions of arsenic tribromide in acetic acid showed exact agreement with the additive law. On the other hand solutions of bromine in acetic acid showed a small departure from the law of additivity, the observed values being slightly greater than the calculated values.

Equal volumes of arsenic tribromide and bromine solutions in acetic acid containing the same concentration of the solute in gram molecules per litre, were mixed together. The density of the mixture was slightly greater than the mean density of the solutions, showing a small contraction in the total volume on mixing. The observed values of the magnetic susceptibility of the mixtures were less (by 4·5 to 1·5% at different decreasing concentrations) than the corresponding calculated values.

This departure from additivity may be attributed to the possible combination of arsenic tribromide and bromine to form arsenic pentabromide. Calculated susceptibility changes generally support this idea. A close association of arsenic tribromide molecules and bromine molecules to form bimolecular complexes, appears very possible in view of the large dipole moment of the interacting molecules.

Attention is drawn to the molecular susceptibility of arsenic tribromide and to the possible presence of a slightly partial double bond in addition to the single covalent bond between arsenic and each of the attached atoms.

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THERMOMAGNETIC PROPERTIES OF MAGNESIUM, SILVER AND LITHIUM

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1. Introduction

In a previous paper, the authors (1941) studied the magnetic susceptibility of strontium at different temperatures in the range from 0°C. to 260°C. The variation was explained on the basis of Stoner's (1936) equation for $(\chi_A)_e$, the electronic contribution to the gram atomic susceptibility of the metal.

$$(\chi_A)_e \times 10^6 = 64{\cdot}21\, n\,(V_0)\left[1 + 1{\cdot}222 \times 10^{-8} T^2 \left\{\frac{1}{n}\frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n}\frac{\partial n}{\partial V}\right)^2\right\}_{V=V_0}\right]$$

Here n (V) is the number of states for one direction of spin per atom per volt, T is the absolute temperature and V_0 is the maximum Fermi energy in volts.

The present work is a continuation of the above study. The metals now investigated are magnesium, silver and lithium.

Magnesium has been investigated by Honda (1910). The two specimens used by him had a comparatively large iron content. The specific susceptibility at infinite field strength was found to have the value of +0·55.* The specific susceptibility of a specimen was found to be 2·22 at 0°C. On heating the specimen, this value decreased slowly at first and more rapidly later until the temperature of 550°C. was reached.

Above 550°C. the specific susceptibility decreased gradually without showing any appreciable change at 630°C., the approximate melting point of magnesium. Attention was drawn by Honda to the fact that at the melting point, the specific susceptibility of the metal was the same as +0·55, the value obtained by extrapolation for the specific susceptibility of the metal at room temperature. The correct procedure would obviously be to determine the specific susceptibility at different field strengths for each temperature and to determine the extrapolated values at different temperatures. It was believed that a careful re-examination of this problem

* All susceptibility values in this paper are given in 10^{-6} unit.

might be of use in studying these results in the light of our present theoretical knowledge. Owen (1912) found the susceptibility of magnesium to vary from +2 to +0·9 in the range of field strength 10 to 25 kilogauss. The extrapolated value at infinite field strength was found to be +0·31. When the temperature of the metal was raised from −170°C. to +20°C. the specific susceptibility decreased from +2·3 to about +1·45. This result is not by itself of any significance since the correction for the ferromagnetic impurity at each temperature is uncertain. Also, it is difficult to reconcile the conclusions of Owen who found that the specific susceptibility decreased rapidly below 20°C. and those of Honda who found a decrease of susceptibility above 0°C.

The diamagnetism of silver is of special interest from the point of view of the magnetic susceptibility contribution by the free electrons in the metal. Honda (1910) found the diamagnetic susceptibility of silver to increase from −0·167 at 0°C. to about −0·19 at 960°C., the melting point of silver. The value increased to about −0·22 on melting. Owen (1912) obtained −0·192 for the specific susceptibility of silver. There was a small but definite increase in the diamagnetic susceptibility when silver was heated from −180°C. to +20°C.

The susceptibility of lithium is of special interest since the contribution by the ion core Li^+ is according to Angus (1932) only −0·7. Almost the entire susceptibility in this element may be taken to be due to the contribution by the conduction electron occupying the $2s$ level. A study of the susceptibility of lithium will be of great utility from the point of view of the paramagnetism of the free electrons. Honda (1910) studied the susceptibility of sodium and potassium. Owen (1912) determined the susceptibilities of lithium, sodium, potassium, rubidium and caesium. His value for the specific susceptibility of lithium is 0·5. He investigated two Kahlbaum specimens and one sample from Merck. Of the Kahlbaum metals, one had a value of +0·50 which was independent of the field intensity and the other had values ranging from +10·06 to +3·36 when the intensity of the field was varied from 5 to 15 kilogauss. At infinite field this gave a value of +0·25. The susceptibilities of the Merck specimen varied from +5·1 to +3·8 in the range from 10 to 25 kilogauss, giving a value of +3·1 at infinite field strengths.

Rao and Sriraman (1937) reinvestigated the susceptibility of lithium by the Curie method, taking special care to eliminate occluded gases from the metal. The susceptibilities were determined at different field strengths from about 4 to 7 kilogauss. The mean paramagnetic susceptibility of

about eight specimens was found to be +2·6. This value brought the paramagnetism of lithium into harmony with the magnetic properties of the other alkali elements.

The temperature variation of the alkali elements is of special interest. Sucksmith (1926) observed a small increase of paramagnetic susceptibility with temperature in the cases of sodium, potassium, rubidium and caesium. Stoner (1935) has accounted for this variation in a satisfactory manner. On account of its large paramagnetism, lithium is specially suitable to verify the theoretical aspects of the question.

2. *Experiment*

Magnesium was available in the form of a wire. A chemical analysis of the metal was carried out by dissolving a known weight (about 20 mg.) in acetic acid and precipitating the magnesium as its 8-hydroxiquinolate $Mg(C_9H_6ON)_2, 2H_2O$. The percentage purity was found to be $100{\cdot}3 \pm 0{\cdot}5$, thus indicating that the purity of the magnesium used was not less than 99·8%.

The magnesium wire was superficially cleaned by immersion in very dilute nitric acid. It was then cut into small bits. About 10 to 15 mg. of the metal was introduced into a small bulb blown at the end of a narrow glass tube. The tube was evacuated with the aid of a Cenco hyvac pump and the bulb was sealed off. Several bulbs were prepared in this manner and only those which showed a comparatively small iron content were used for the thermomagnetic study.

Two specimens of silver were available, one of which was of A.R. quality from Kahlbaum. The other was also of high purity. In view of the fact that the diamagnetic susceptibility of silver agreed with those of other workers, no attempt was made to determine the percentage purity of silver by any chemical method.

A chemical analysis of lithium metal was carried out by dissolving a known weight (about 50 mg.) in double distilled water, adding excess of N/10 hydrochloric acid and titrating the excess against N/100 sodium hydroxide solution. A solution of rosalic acid (0·1%) in conductivity water was used as the indicator.

The percentage purity of the specimen was $99{\cdot}9 \pm 0{\cdot}2$. It may be therefore taken that the metal employed had a purity not less than 99·7%. Bulbs of pyrex glass containing about 10 to 20 mg. of lithium were prepared by the method adopted by Rao and Sriraman (1937).

Determination of the susceptibility.—The magnetic susceptibilities of the elements were determined by the Curie method.

If d_s and d_w be the deflections obtained for any metal and water respectively, it may be shown that

$$\frac{d_s}{d_w} = \frac{k_s v_s - k_a v_i}{k_w v_w - k_a v_i'},$$

where k_s and k_w are the volume susceptibilities of the substance and water respectively, v_s and v_w their volumes, k_a the volume susceptibility of the surrounding air and v_i and v_i' the internal volumes of the bulbs containing the substance and water.

Let m_s, m_w and χ_s, χ_w be the masses and specific susceptibilities of the substance and water respectively.

Then,

$$\frac{d_s}{d_w} = \frac{m_s \chi_s - k_a v_i}{m_w \chi_w - k_a v_i'}.$$

The volume susceptibility of air at N.T.P. is $+0{\cdot}029$ (*Int. Crit. Tables*, 1929). For a paramagnetic gas, the volume susceptibility varies directly as the square of the absolute temperature. The volume susceptibility of air at atmospheric pressure and at 30° C. is found to be $+0{\cdot}036$. The bulbs prepared had an internal diameter of nearly 4 mm. which gives for the internal volume, a value of about 0·032 c.c. Hence, $k_a v_i$ becomes $0{\cdot}036 \times 10^{-6} \times 0{\cdot}032$ or $0{\cdot}00115 \times 10^{-6}$. At 330° C. this value would work to about $0{\cdot}0046 \times 10^{-6}$. In the case of magnesium and lithium, this correction works out to be a negligibly small amount. In the case of silver however, since $m_s \chi_s$ is small, due account was taken of the volume susceptibility of air.

The mass of water m_w for each calibration was arranged to have such a value that d_s may be very nearly equal to d_w. $m_w \chi_w$ was thus made nearly equal to $m_s \chi_s$.

In the case where the volume susceptibility of air was neglected,

$$\frac{d_s}{d_w} = \frac{m_s \chi_s}{m_w \chi_w}$$

or

$$\chi_s = \frac{m_w}{m_s} \times \frac{d_s}{d_w} \times \chi_w.$$

Correction for the presence of ferromagnetic impurities.—Honda's (1910) equation $\chi_i = \chi_p + \sigma m_i / H$ was employed to eliminate the influence of the ferromagnetic impurity. In the present investigation, the specific susceptibility

χ_i was determined at different field currents for every metal and at each temperature investigated. In each case, a graph was drawn between χ_i and 1/H. The points plot themselves on a straight line. On producing the straight line, the susceptibility when 1/H is zero, could be determined.

Heating arrangement.—The bulbs containing the metals were studied at different temperatures by enclosing each of them inside a narrow cylindrical heater. The electric heater employed, was made by winding constantan wire around a cylinder of thin plate copper, asbestos paper being used for insulation. The winding was made non-inductive and test experiments showed that no sensible change of the magnetic field inside the heater was produced because of the heating wire. The pole pieces were cooled by cotton wads drenched with ice water. The details of the experiment were similar to those adopted with strontium.

In all the metals studied, susceptibilities were determined only up to 270° C. At higher temperatures, convection currents were set up and the readings could not be taken with any reliability. A vacuum Curie balance would be ideal for the purpose both for the determination of susceptibility at high and at low temperatures. Experiments in this direction are now in progress.

3. *Results*

(*a*) *Metals at room temperature*

(*i*) *Magnesium.*—In view of the comparatively large iron content in the case of magnesium, the magnetic susceptibility at the room temperature was determined with eight specimens of the metal. The readings are tabulated in Table I.

The average specific susceptibility of magnesium is found to be $+1{\cdot}08\pm 0{\cdot}08$. The gram atomic susceptibility of the metal is therefore $24{\cdot}30\times 1{\cdot}08$ or 26·2. The value of the specific susceptibility of magnesium obtained in this investigation is much larger than $+0{\cdot}55$ obtained by Honda (1910) and $+0{\cdot}263$ by Owen (1912). The exact purity of the specimens used by them was not accurately determined. Also when graphs are drawn between χ and H, extrapolation for infinite field strength becomes uncertain particularly when the specific susceptibilities at the field strengths employed are large because of considerable ferromagnetic impurity. One is inclined therefore to attribute the low value of the specific susceptibility of magnesium obtained by the early workers to an overcorrection for this impurity.

In χ, 1/H graphs, straight lines are obtained and hence the extrapolated values are more reliable.

TABLE I

Bulb No.	Mass mg.	Current amps.	χ_i	Extrapolated χ_p
1	16·2	2	5·56	
		3	3·82	1·05
		4	3·09	
		5	2·82	
2	18·3	2	5·80	
		3	4·10	1·15
		4	3·31	
		5	3·07	
3	16·7	2	5·76	
		3	4·08	1·17
		4	3·27	
		5	3·05	
4	23·8	2	5·87	
		3	3·94	1·12
		4	3·27	
		5	2·94	
5	19·2	2	5·97	
		3	4·02	1·04
		4	3·28	
		5	2·99	
6	17·7	2	5·19	
		3	3·43	1·02
		4	2·84	
		5	2·70	
7	19·0	2	5·37	
		3	3·60	1·00
		4	2·94	
		5	2·67	
8	23·5	2	4·87	
		3	3·47	1·12
		4	2·89	
		5	2·68	

(*ii*) *Silver.*—The results for three specimens of silver are tabulated below.

TABLE II

Specimen No.	Mass mg.	Current amps.	χ_i	Extrapolated χ_p
1	210·0	1	−0·136	
		2	−0·164	−0·184
		3	−0·172	
		4	−0·179	
2	327·6	1	−0·130	
		2	−0·162	−0·182
		3	−0·170	
		4	−0·173	
3	417·0	2	−0·104	
		3	−0·138	−0·185
		4	−0·147	

The mean specific susceptibility of silver is found to be $0\cdot184 \pm 0\cdot002$. This result agrees closely with $-0\cdot1794$ obtained by Vogt (1932) and $-0\cdot1863$ by Svensson (1932). The values of $-0\cdot205$ and $-0\cdot201$ given by Honda (1910) and Owen (1912) respectively are definitely higher than the most probable value.

(*iii*) *Lithium.*—The results obtained with two specimens are given below.

TABLE III

Specimen No.	Mass mg.	Current amps.	χ_i	Extrapolated χ_ρ
1	4·5	1	6·42	2·54
		2	4·03	
		3	3·32	
		4	3·18	
2	11·3	1	3·12	2·50
		2	2·81	
		3	2·60	
		4	2·55	

Since the value obtained here agrees with the mean value of $+2\cdot6$ obtained by Rao and Sriraman (1937), more specimens were not studied particularly since the aim of the present investigation was to study the temperature variation of the specific susceptibility of lithium. The only other value for lithium for comparison is that of Owen (1912) who obtained $+0\cdot5$. His value however suffers from an uncertainty in the correction for the ferromagnetic impurity.

(*b*) *Susceptibility variation with temperature*

(*i*) *Magnesium.*—Under very reliable conditions, two runs were made with specimen number 8 of Table I. The specific susceptibility at room temperature of this specimen was $+1\cdot12$. Another experiment was carried out with specimen number 4 of Table I, whose susceptibility at 30° C. was also $+1\cdot12$.

The results are tabulated in Table IV.

TABLE IV

Specimen number 8				Specimen number 4	
I Run		II Run			
Temperature °C.	Susceptibility	Temperature °C.	Susceptibility	Temperature °C.	Susceptibility
30	1·12	30	1·12	30	1·12
76	1·10	76	1·12	76	1·10
103	1·09	103	1·08	103	1·07
134	1·01	134	1·04	134	1·02
166	1·00	166	1·01	166	1·00
197	0·98	197	0·96	197	0·96
230	0·95	230	0·95	230	0·94
270	0·92	270	0·89	270	0·92

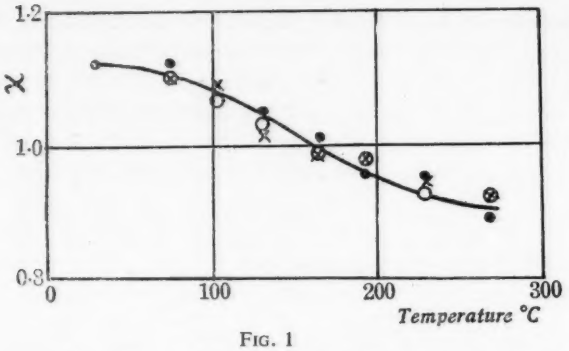

FIG. 1

Fig. 1 shows the graph between the specific susceptibility of magnesium and temperature. The susceptibility is found to decrease with temperature, at first slowly and a little more rapidly above 100° C. The fall in the susceptibility value however is less than in the case of strontium.

(*ii*) *Silver*.—The results obtained with a specimen are given below. It will be observed that in the temperature range investigated, the susceptibility remains sensibly constant.

TABLE V

Temperature °C.	Susceptibility	Temperature °C.	Susceptibility
30	−0·184	166	−0·183
76	−0·184	197	−0·184
103	−0·186	230	−0·185
134	−0·184	270	−0·185

The approximate constancy of the specific susceptibility of silver in the temperature range investigated agrees with the conclusions of Honda (1910) and Owen (1912). The agreement on this point tends to confirm the reliability of the observations made in the present investigation.

(*iii*) *Lithium*.—In view of the relatively large ferromagnetic content in this metal, accurate measurements were made of the deflections at different field currents for each temperature investigated. The results at two temperature runs are given in Table VI.

TABLE VI

Temperature °C.	Susceptibility	Temperature °C.	Susceptibility
30	2·50	30	2·50
76	2·52	76	2·52
103	2·54	120	2·55
134	2·55	150	2·55
166	2·56	182	2·57
197	2·41	197	2·43
230	2·40	214	2·42
270	2·42	230	2·44

These results are plotted in Fig. 2. It is seen that as the temperature increases from 30° C., there is a small but definite increase in the susceptibility value to about $+2{\cdot}57$ at 186° C., the melting point of lithium. At this temperature there is a fall in the susceptibility from 2·57 to 2·42. As the temperature is raised still further, there is a small increase in the susceptibility value.

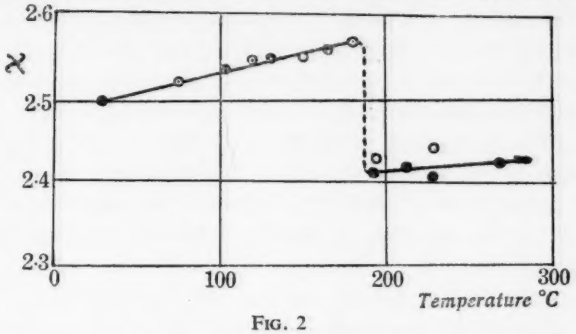

FIG. 2

In this respect the behaviour of lithium is similar to that of the other alkali elements investigated by Sucksmith (1926).

4. *Discussion*

(*i*) *Magnesium.*—The gram atomic susceptibility of magnesium is found here to be $+26{\cdot}2$. The gram ionic susceptibility of magnesium according to Kido (1933) is $-4{\cdot}3$. It is thus found that the contribution to the susceptibility of a gram atom of the metal by the valence electrons (two per atom) is equal to $+30{\cdot}5$ in the case of magnesium. From the equation

$$(\chi_A)_e = \frac{32{\cdot}1q}{V_0}$$

where q is 2 for the atom in question, V_0 is found to be 2·1 volts.

Table VII gives the values of V_0, the width in volts of the occupied energy range in the completely degenerate state of the valence electrons, in the cases of magnesium, calcium, strontium and barium.

TABLE VII

Metal	Author	χ_A for metal	$(\chi_A)_i$ for ions	$(\chi_A)_i$ for electrons	V_0 in volts
Mg	Honda (1910)	13·4	−4·3	17·7	3·6
	Owen (1912)	6·2	−4·3	10·5	6·1
	Authors	26·2	−4·3	30·5	2·1
Ca	Owen (1912)	44·1	−6·5	50·6	1·3
Sr	Owen (1912)	−17·5	−15·6	−1·9	?
	Rao and Savithri (1941)	92·0	−15·6	107·6	0·6
Ba	Owen (1912)	123·6	−23·6	147·2	0·44
	Lane (1933)	19·9	−23·6	43·5	1·50

An examination of the above table shows how divergent are the values of V_0 for a given metal when worked out from the results of different observers. It has already been mentioned that the gram atomic susceptibility values for magnesium obtained by Honda (1910) and Owen (1912) are too low, probably due to an overcorrection for ferromagnetic impurities. The values of V_0 calculated from their results appear to be too high.

The result for calcium by Owen (1912) appears to be quite reasonable. But it is clear from Owen's paper that the ferromagnetic content in the specimen of calcium used by him should have been very high. In fact the specific susceptibility decreased from about + 70 to about + 40 in the range of field strength 7 to 13 kilogauss. It is obvious that any kind of extrapolation from such remote conditions should be accompanied by considerable error. It seems therefore necessary to redetermine the susceptibility of calcium.

(*ii*) *Temperature variation of the susceptibility of magnesium.*—The temperature variation of the specific susceptibility of the elements of this group is intimately connected with the Fermi energy distribution of the valence electrons. For strictly free electrons, Stoner (1935) has shown that when the absolute temperature T is much less than $1 \cdot 157 \times 10^4 \times V_0$ (where V_0 is the energy width in volts of the occupied states in the completely degenerate state), the gram atomic susceptibility $(\chi_A)_e$ due to the free electrons is expressed by

$$(\chi_A)_e \times 10^6 = \frac{32 \cdot 1q}{V_0}\left[1 - 6 \cdot 11 \times 10^{-9}\left(\frac{T}{V_0}\right)^2\right].$$

This expression indicates that in the case of perfectly free electrons, the gram atomic susceptibility due to these electrons should show a small decrease with temperature.

It will be clear from section (1) above, that in the case of magnesium and strontium, the electron energy bands are much narrower than for free electrons. Hence the above expression will not strictly apply to these cases.

The two valence electrons in the metal under consideration may be considered to be loosely bound. In magnetic properties, strontium and magnesium seem to behave like the rare earth elements. They have a comparatively high paramagnetism. An account of the spin paramagnetism of the rare earths is given by Wilson (1939). In the absence of a magnetic field, the number of free electrons with their spins along the direction of the field is equal to the number with their spins in the opposite direction. The effect of the applied magnetic field is to increase the former and decrease the latter. The reversal of spin increases the kinetic energy of such electrons which go into higher energy states which were unoccupied. It is found

therefore that the electrons near the top of the Fermi distribution really contribute to the paramagnetism in these cases.

These points are rendered clearer if we picture schematically the relation between the number of states per unit energy range $n(\epsilon)$ and energy ϵ. In the simplest case, when the atoms (as in the case of the alkali elements) have only one loosely bound electron, it would be enough if only the first band is considered since there are electrons in these cases just enough to fill up only a part of this band. The electrons near the top of the Fermi distribution would really contribute to the paramagnetism in this case.

With divalent elements, the loosely bound electrons may occupy a larger portion of the first band. Further, there is the second band to be considered in the case of the rare earths and the alkaline earth metals. In the case of semi-conductors, there will be no overlapping of the first and second band. But in the case of conductors, an overlapping should take place. We should assume that such an overlap should occur in the case of the alkaline earth metals since they are moderate conductors. The top of the Fermi distribution may come somewhere after the region of overlapping. Attention was drawn in Art. 1 to the following formula (of Stoner, 1936) for $(\chi_A)_e$ the electronic contribution to the gram atomic susceptibility.

$$(\chi_A)_e \times 10^6 = 64{\cdot}21\ n\ (V_0)\left[1 + 1{\cdot}222 \times 10^{-8}\ T^2 \left\{\frac{1}{n}\frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n}\frac{\partial n}{\partial V}\right)^2\right\}_{V=V_0}\right]$$

The spin susceptibility will increase or decrease with temperature in the low temperature range as the sign of the quantity

$$\left\{\frac{1}{n}\frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n}\frac{\partial n}{\partial V}\right)^2\right\}_{V=V_0}$$

is positive or negative.

When there is overlapping of two bands as in the case of the alkaline earth elements, the sign of the temperature coefficient of susceptibility will depend on the extent of overlapping. The high paramagnetism of magnesium shows that this overlapping must be considerable. It is of interest that in exactly such a case the temperature coefficient of the paramagnetism due to electrons assumes importance.

In the case of magnesium, the paramagnetic susceptibility of the loosely bound electrons is found to decrease with temperature showing that in this case,

$$\left\{\frac{1}{n}\frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n}\frac{\partial n}{\partial V}\right)^2\right\}_{V=V_0}$$

is negative.

That the energies of the conduction electrons lie within a range of values and that the unoccupied and occupied states are divided into bands, have

obtained a direct proof from experiments on the fine structure studies of some emission lines in the soft X-ray region carried out by O'Bryan and Skinner (1934). The K emission bands of lithium and beryllium and the L_{III} bands of magnesium and aluminium were investigated with a high vacuum, soft X-ray ruled grating spectrograph. In the case of lithium and beryllium a single band was obtained with a sharp cut off on the high energy side representing the top of the Fermi distribution. States with kinetic energy greater than the Fermi maximum were thus shown to be empty. The emission band obtained with magnesium showed clear evidence of the existence of conduction electrons in two zones. The breadths of the bands for the metals investigated measured in volts agreed with the values for the maximum Fermi energy calculated by Sommerfeld (1928).

(*iii*) *Temperature variation of the susceptibility of lithium and silver.*— The gram atomic susceptibility of lithium in the present investigation is found to be $6{\cdot}94 \times 2{\cdot}5$ or $17{\cdot}35$. The ionic susceptibility of a gram atom of lithium is according to Kido (1933), $-1{\cdot}6$. But it has been shown by Hoare and Brindley (1934), (1935) and by Angus (1932) that the ionic susceptibility of Li^+ is $-0{\cdot}7$. Taking the latter value as the more reliable, the paramagnetic susceptibility of the free electrons in a gram atom of lithium is found to be $18{\cdot}05$. The value of V_0 the width in volts of the energy band for the free electrons works out to be

$$V_0 = 32{\cdot}1/(\chi_A)_e = 32{\cdot}1/18{\cdot}05 = 1{\cdot}78 \text{ volts.}$$

This indicates according to Stoner (1934) a narrowing of the energy band. In this respect, lithium resembles the other alkali metals. Rao and Sriraman (1937) presented a table comparing the values of V_0 for the different alkali metals, with those calculated on the basis of the formula of Sommerfeld (1928) for the maximum Fermi energy.

The temperature variation of the susceptibility of the alkali elements has been considered by Stoner (1935). He has drawn attention to the fact that for the alkali metals, the conditions approach most closely those for which the free electron calculations should apply. He has suggested that the increase of susceptibility for the alkali elements should be mainly due to the change in the value of V_0 due to thermal expansion. His calculations show that

$$V_0 \propto n_v^{2/3}$$

where n_v is the number of ions per unit volume. Let α_v be the coefficient of cubical expansion. Then

$$(\chi_A)_e \propto \frac{1}{V_0} \propto n_v^{-2/3} \propto 1 + \frac{2}{3}\alpha_v T.$$

Hence

$$\Delta\ (\chi_A)_e/(\chi_A)_e \Delta T = \frac{2}{3}\ \alpha_v.$$

The temperature coefficient of the paramagnetic contribution of the free electrons is found to be nearly equal to two-thirds of the coefficient of cubical expansion. This conclusion was verified by Stoner (1935) with the results for the alkali elements obtained by Sucksmith (1926). In the case of lithium, the paramagnetic contribution of the free electrons in a gram atom works to 18·05 at 30°C. and 18·54 at 180°C. The temperature coefficient is calculated to be $1{\cdot}8 \times 10^{-4}$. The value of $2\alpha_v/3$ for lithium is $1{\cdot}0 \times 10^{-4}$ calculated from the data for the coefficient of linear expansion of this metal given in *Int. Crit. Tables*, II, p. 461. There is thus found to be good agreement supporting Stoner's theory.

The gram atomic susceptibility of silver is $107{\cdot}88 \times -(0{\cdot}184)$ or $-19{\cdot}9$. Taking the ionic susceptibility of silver to be $-26{\cdot}2$ after Kido (1933), the susceptibility of the valence electron in a gram atom of the metal is found to be $+6{\cdot}3$. The value of V_0, the width of the energy band in this case becomes $32{\cdot}1/6{\cdot}3$ or 5·1 volts. The value of the maximum Fermi energy according to the formula of Sommerfeld (1928) is found to be 5·52 volts. (See Mott and Jones, 1936, p. 54.) There is a close agreement between the values of the band width calculated by the two methods. It may therefore be concluded that the valence electron in silver approximates to the condition of a free electron.

One would expect therefore, that experiments with silver would verify Stoner's formula mentioned above. Unfortunately the value of the paramagnetic susceptibility of the valence electrons in silver is quite small and the temperature range from 30° C. to 270° C. was not large enough. Hence a clear proof of Stoner's formula could not be had from the data obtained with silver since it was found that the susceptibility of silver did not show any appreciable variation in the temperature range investigated.

5. Summary

The specific magnetic susceptibilities of magnesium, lithium and silver have been determined by the Curie method at different temperatures in the range 30° to 270° C.

The specific susceptibility of magnesium at 30° C. was found to be $+1{\cdot}08 \times 10^{-6}$ contrary to the low values of $+0{\cdot}263 \times 10^{-6}$ and $+0{\cdot}58 \times 10^{-6}$ obtained by Honda and Owen respectively. When the temperature of magnesium is raised, the specific susceptibility is found to decrease slowly in the region from 30° C. to 100° C. and a little more rapidly in the range

from 100° to 270° C. It has been pointed out that magnesium behaves like the rare earth elements.

The specific susceptibility of lithium at 30° C. was found to be $2{\cdot}5 \times 10^{-6}$ in agreement with the value of Rao and Sriraman (1937). The susceptibility shows a small but definite rise in value when heated from $2{\cdot}50 \times 10^{-6}$ at 30° C. to $2{\cdot}57 \times 10^{-6}$ at 186° C. the melting point of lithium. At this temperature, there is a fall in the susceptibility value from $2{\cdot}57 \times 10^{-6}$ to $2{\cdot}42 \times 10^{-6}$. As the temperature is raised still further, there is a small increase in the susceptibility value. The variation of the susceptibility contribution of the valence electron with increase of temperature is in full agreement with the theory of Stoner and the experimental results obtained by Sucksmith for sodium, potassium, rubidium and caesium.

The gram atomic susceptibility of silver was found to be $-19{\cdot}9 \times 10^{-6}$. This gave for the width of the energy band of the free electrons a value of 5·1 volts in agreement with 5·52 volts calculated for the maximum Fermi energy by Sommerfeld. The valence electron in silver may be taken therefore to approximate very closely the ideal condition of a free electron. The specific susceptibility of silver was found to remain sensibly constant in the temperature range from 30° C. to 270° C. This observation does not show any disagreement with Stoner's theory since the change of susceptibility on the basis of this theory in the temperature range investigated will be well within the errors of experiment.

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MAGNETIC SUSCEPTIBILITY OF SOME PEROXIDES

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1. Introduction

The magnetic properties of metallic oxides do not seem to have been investigated in any complete or systematic manner. Considerable differences are often found in the values of magnetic susceptibility for any oxide, obtained by different investigators. A thorough and extensive study of the magnetic susceptibility of carefully analysed metallic oxides seems desirable. In this paper, the magnetic susceptibilities of hydrogen peroxide, sodium peroxide and barium peroxide have been determined. These peroxides do not seem to have been investigated before. But in a paper by Grey and Farquharson (1930), attention has been drawn to the experimentally determined value of $-(16{\cdot}73 \pm 0{\cdot}20)$* by Farquharson for the molecular diamagnetic susceptibility of hydrogen peroxide. Grey and Farquharson (1930) discussed the molecular structure of hydrogen peroxide from the magnetic point of view.

A peroxide may be considered strictly as an oxide containing more oxygen united to a certain quantity of an element than is contained in its highest typical oxide, according to the periodic law. Na_2O_2 and BaO_2 are true peroxides.

Mendeleef suggested a manner of classification of peroxides on structural grounds depending on the valency of the element united to oxygen. The oxygen atom or atoms over and above those required to form the basic oxide may either be doubly linked to the metal atom or singly linked to the metal and to oxygen forming a chain and so preserving the valency of the metal in the basic oxide unchanged.

2. Experiment

(*a*) *Hydrogen peroxide.*—Perhydrol was available in paraffined bottles from Merck. The bottles were labelled to contain 30% by weight of H_2O_2. But quantitative analysis showed that the concentration of the specimens was about 28%.

* Susceptibility values in this paper are in 10^{-6} unit.

This sample was diluted with fresh double distilled water to obtain different concentrations. The accurate concentration at any dilution was determined by titration against approximately N/10 potassium permanganate solution standardised with A.R. KHC_2O_4, $H_2C_2O_4$, $2H_2O$ solution of accurately known concentration. A sample with 32% H_2O_2 was prepared by concentrating the stock solution in a vacuum desiccator.

The magnetic susceptibility of the peroxide solutions was determined by the Gouy method, using water as the standard substance. The relative densities of the solutions were found by weighing equal volumes of the solutions and of water.

(*b*) *Sodium peroxide.*—The sodium peroxide available was a specimen of the 'Analar Analytical Reagent'. The maximum limits of impurities specified are the following :—Chloride (Cl) 0·04%; Sulphate (SO_4) 0·005% ; Phosphate (PO_4) 0·005%; Silicate (SiO_2) 0·01%; Heavy metals (Pb) 0·01% ; and Iron (Fe) 0·005%.

The chemical analysis for the percentage purity of the peroxide in the specimen was carried out by using standardised potassium permanganate solution and boric acid. The sodium peroxide available was found to have a percentage purity of 94·0. The remaining part of the substance, except for small impurities stated above, should be the monoxide of sodium (Na_2O).

Specimens having a smaller peroxide content were prepared by heating the above stock substance *in vacuo*. It was not, however, possible to reduce the concentration to less than about 65%.

The specific susceptibility of the peroxide was determined by the Curie method.

(*c*) *Barium peroxide.*—The barium peroxide available was a specimen from Kahlbaum. The percentage purity of the peroxide was determined by using standardised permanganate solution and hydrochloric acid. The percentage purity of the available specimen was found to be 86·4%.

That the remaining quantity (13·6%) consists of BaO was confirmed by determining the barium content of the available substance by dissolving the peroxide in hydrochloric acid and precipitating barium sulphate. These tests showed that the given substance apart from any impurity traces contained 86·4% of barium peroxide (BaO_2) and 13·6% of the monoxide (BaO).

3. Results

(*a*) *Hydrogen peroxide.*—The results obtained with hydrogen peroxide at different concentrations are given in Table I. Column 1 gives the

concentration of hydrogen peroxide in the solution expressed in grams weight of the peroxide in 100 grams of the solution. Column 2 gives the number of concentrations studied in the neighbourhood of the concentration value indicated in column 1, the range in the percentage concentration being less than 1. Column 3 gives the density values determined by the method of weighing equal volumes of the liquids. The fourth column gives the volume susceptibility, being the mean of the values obtained for field currents of 2, 3, 4 and 5 amperes. Since the susceptibility values were nearly equal for different field currents, it was concluded that there was no ferromagnetic impurity in the liquid studied.

The fifth column gives the specific susceptibility values, χ being equal to κ/ρ. Assuming the specific susceptibility of water to be $-0{\cdot}720$, the specific susceptibility of the hydrogen peroxide was calculated in each case and the values are shown in the last column.

TABLE I

Concentration	No. of concentrations studied	Mean density ρ	Mean volume susceptibility κ	Mean specific susceptibility χ	$\chi_{H_2O_2}$
6·5	3	1·032	−0·739	−0·716	−0·658
8·7	2	1·041	−0·742	−0·713	−0·640
10·9	2	1·049	−0·743	−0·708	−0·610
12·7	4	1·054	−0·745	−0·700	−0·617
14·7	2	1·061	−0·747	−0·704	−0·611
16·5	2	1·066	−0·749	−0·703	−0·617
21·3	1	1·077	−0·754	−0·700	−0·626
28·1	3	1·092	−0·757	−0·693	−0·624
32·0	1	1·100	−0·760	−0·691	−0·630

At the first two concentrations studied, the specific susceptibility of hydrogen peroxide is found to be higher than in the subsequent cases. Due to the small concentrations taken, there is likelihood of a large error in the value of the specific susceptibility in the first two cases. With the evidence available, it is difficult to say whether the large value of the specific susceptibility of the peroxide at very low concentrations is a genuine effect.

The mean of χ taking into account concentrations above 10%, is found to be $-0{\cdot}619$. The values range from $-0{\cdot}610$ to $-0{\cdot}630$. Thus χ may be taken to be $-(0{\cdot}619 \pm -0{\cdot}011)$.

The molecular susceptibility of hydrogen peroxide is therefore found to be $-(21{\cdot}0 \pm 0{\cdot}4)$. Grey and Farquharson (1930) report that Farquharson's

experiments gave for the molecular diamagnetism of hydrogen peroxide the value $-(16{\cdot}73 \pm 0{\cdot}20)$. This value is much lower than the value obtained in the present investigation. No details of experiment are presented by Farquharson. Considering the large number of independent measurements made here, and the close uniformity of the values arrived at, it appears that $-(21{\cdot}0 \pm 0{\cdot}4)$ is reliable.

(*b*) *Sodium peroxide.*—The A.R. sodium peroxide available was found to have a percentage purity of 94. It is obvious that the remaining 6% should consist of Na_2O.

Since the peroxide contained a small ferromagnetic impurity, it was essential to determine the specific susceptibility of any sample at different field currents. If χ_i is the specific susceptibility of an impure specimen containing ferromagnetic impurity and χ_p that of the pure specimen,

$$\chi_i = \chi_p + \sigma m/H,$$

where σ is the specific intensity of magnetisation of the impurity, m the mass of the impurity in one gram of the substance, and H the field strength. For each of the specimens studied, a graph was drawn between χ_i and 1/H. By extrapolation the value of χ_i at infinite field strength was determined.

The results obtained with four specimens containing different percentages of sodium peroxide are given in Table II.

TABLE II

Field current in amperes	Percentage of composition by weight of peroxide			
	64·9	70·1	77·2	94·0
2	−0·297	−0·283	−0·288	−0·313
3	−0·317	−0·310	−0·313	−0·330
4	−0·325	−0·320	−0·325	−0·338
5	−0·328	−0·324	−0·328	−0·341
$\chi_p = (\chi_i)_{H\to\infty}$	−0·346	−0·348	−0·350	−0·358

Assuming that each specimen contained only the peroxide and monoxide of sodium and neglecting the minute traces of non-ferromagnetic impurities, the results of Table II give for the specific susceptibilities of the peroxide and the monoxide, the values of $-0{\cdot}36$ and $-0{\cdot}32$ respectively.

Table III shows the values of the specific susceptibilities of the peroxides investigated.

TABLE III

Percentage of peroxide	χ Calculated	χ Observed
64·9	−0·346	−0·346
70·1	−0·348	−0·348
77·2	−0·351	−0·350
94·0	−0·358	−0·358

As a matter of fact, the χ values of Na_2O and Na_2O_2 were calculated from the specific susceptibilities at concentrations of 64·9 and 94·0 on the principle of two simultaneous equations involving two unknown quantities. These values are found to fit very well the other two specimens investigated.

The molecular susceptibility of Na_2O_2 works out to be $-78 \times 0{\cdot}36$ or $-28{\cdot}1$. That of Na_2O is found to be $-62 \times 0{\cdot}32$ or $-19{\cdot}8$.

(*c*) *Barium peroxide.*—It was mentioned in article 2 (*c*) that the available specimen had a percentage purity of 86·4. By heating a small quantity of the substance *in vacuo* in a hard glass test tube, the percentage purity of the peroxide could be reduced. Specimens with different peroxide contents were prepared in this manner and studied. Besides barium peroxide the substance contained barium monoxide. When the peroxide is heated, part of it gives up oxygen and is converted into the monoxide.

The specific susceptibility of barium monoxide (BaO) was determined directly by the Curie method using a pure specimen available from Kahlbaum. The mean value obtained was $-0{\cdot}19$.

The results obtained with six specimens of barium peroxide are given below.

TABLE IV

Field current in amperes	Percentage composition by weignt of peroxide					
	70·6	71·8	73·8	78·3	84·5	86·4
2	−0·193	−0·190	−0·205	−0·199	−0·215	−0·212
3	−0·205	−0·203	−0·215	−0·211	−0·222	−0·220
4	−0·211	−0·210	−0·218	−0·215	−0·227	−0·224
5	−0·213	−0·212	−0·219	−0·217	−0·227	−0·226
$\chi_\rho = (\chi_i)_{H\to\infty}$	−0·226	−0·226	−0·228	−0·230	−0·235	−0·235

Assuming the specific susceptibility of BaO to be $-0{\cdot}19$ the specific susceptibility of BaO_2 could be calculated in each of the above six cases. The values of the specifie susceptibility of BaO_2 are tabulated in Table V.

TABLE V

Percentage composition	χ Mixture	χ BaO_2
70·6	−0·226	−0·241
71·8	−0·226	−0·240
73·8	−0·228	−0·241
78·3	−0·230	−0·240
84·5	−0·235	−0·243
86·4	−0·235	−0·242

The mean specific susceptibility of barium peroxide is found to be − 0·24. The molecular susceptibility of the peroxide is equal to − 40·6. That of BaO works to − 29·1.

4. *Discussion*

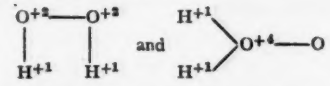
(*a*) *The magnetic susceptibility of the monoxides.*—According to Kido (1933), the ionic susceptibilities of Na^+ and Ba^{++} are − 7·6 and − 23·6 respectively. Rao and Sriraman (1937) have calculated these values from the results of Flordal and Frivold (1935) and have given − 6·9 and − 29·3 as the ionic susceptibilities of Na^+ and Ba^{++} respectively. The ionic susceptibility for O^{--} given by Kido (1933) is − 13·7. This value seems quite reasonable.

From Kido's data, we may calculate the molecular susceptibility of BaO and of Na_2O. The values are found to be − 28·9 for Na_2O and − 37·3 for BaO. The observed values are − 19·8 for sodium monoxide and − 29·1 for barium monoxide. This shows that in the case of sodium monoxide, the binding is accompanied by a paramagnetic component of − 9·1. In the case of barium monoxide this component works to − 8·2.

In the case of water, account will have to be taken of the contribution to the molecular susceptibility by the two hydrogen ions. Although Kido (1933) has taken the susceptibility of H^+ to be zero, Weiss (1930) has advanced satisfactory evidence to the effect that the ion H^+ has an effective paramagnetism of about + 1·1. This would make the susceptibility of water to have the value 11·5 which is not very far from the molecular susceptibility of H_2O molecules.

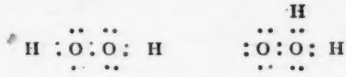
These considerations show that the energies of binding between the metal and oxygen in the monoxides of sodium and barium are quite strong.

(*b*) *Structure of the hydrogen peroxide molecule.*—Grey and Farquharson (1930) considered the structure of the hydrogen peroxide molecule. They considered two alternative structures :



From their results they obtained support for the first formula.

The present view seems to be that hydrogen peroxide may be tautomeric and may be represented electronically in two ways in the following manner :



The first structure may be represented in the following manner.

$$H^{+1} + O^{-2} + O^{-2} + H^{+1}.$$

Assuming the ionic susceptibility of O^{-2} to be $-13{\cdot}7$ according to Kido (1933) and introducing the value $+1{\cdot}1$ for the paramagnetic component of hydrogen after Weiss (1930) we obtain for the molecular susceptibility of this structure the value $-25{\cdot}2$.

If the structure is represented by the second form indicated above, the molecular susceptibility may be calculated from the following :

$$O + O^{-2} + H^{+1} + H^{+1},$$

where O represents neutral oxygen atom. The susceptibility per gram atom of O° may be calculated by the method of Slater (1930) modified by Angus (1932). A calculation shows this to be $-8{\cdot}3$. The molecular susceptibility of the hydrogen peroxide if it possesses the above structure would be $-8{\cdot}3 - 13{\cdot}7 + 1{\cdot}1 + 1{\cdot}1$ or $-19{\cdot}8$.

It is likely that any deformation within the molecule might reduce this value.

If the molecular susceptibility of the above structure is worked by the method of Kido (1933), we have to introduce the value of $-7{\cdot}7$ for the susceptibility of the oxygen ion with the double bond. This would give for the susceptibility per gram atom of hydrogen peroxide the value of $-13{\cdot}7 - 7{\cdot}7 + 1{\cdot}1 + 1{\cdot}1$ or $-19{\cdot}2$. It is seen that the molecular susceptibility of hydrogen peroxide obtained in the present investigation is $-(21{\cdot}0 \pm 0{\cdot}4)$. This value comes intermediate between the values calculated for the two tautomeric constitutions. The observed value however is nearer the value obtained for the second structure.

Penney and Sutherland (1934 *a*) considered the structure of hydrogen peroxide with special reference to electrical moment. Linton and Maass (1932) found the electrical moment of H_2O_2 to be $2{\cdot}13 \times 10^{-18}$ e.s.u. This is a surprisingly large value.

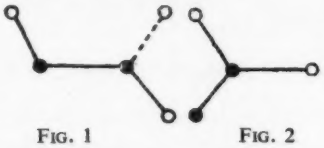


FIG. 1

FIG. 2

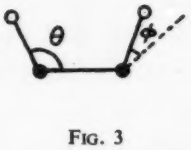


FIG. 3

They concluded that Fig. 2 was the correct model with a semipolar double bond between the two oxygen atoms. Theilacker (1933) suggested the above result supports the structure shown in Fig. 1 if a free rotation of the (OH) groups relative to one another around the O—O line.

Raman effect data by Venkateswaran (1933) favour the H–O–O–H arrangement. He finds the most prominent Raman line to show a shift of 875 cm.$^{-1}$ This order of frequency is just what one would expect for the relative oscillations of 2 (OH) groups bound by single oxygen bond. The form H_2O-O would not give such a frequency.

Penney and Sutherland (1934 *a*) have adopted the H–O–O–H arrangement of the type shown in Fig. 3, θ and ϕ being very nearly 100°.

Sidgwick (1934) observes that one should expect H_2O_2 to have two tautomeric structures H-O-O-H and .

These cannot resonate but both give the same ion H-O-$\bar{O}$.

It must however be mentioned that H_2O_2 is not made up of two $(OH)^{-1}$ ions in loose combination for, since the ionic susceptibility of $(OH)^{-1}$ according to Kido (1933) is $-8{\cdot}5$, the molecular susceptibility of H_2O_2 would work in this case to $-2 \times 8{\cdot}7$ or $-17{\cdot}4$. Our value is much higher, being $-(21{\cdot}0 \pm 0{\cdot}4)$.

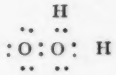
In another paper, Penney and Sutherland (1934 *b*) have determined the most stable configuration of the hydrogen peroxide molecule by the method of electron pairs. Their conclusions support the structure shown in Fig. 3, in which the azimuth of half of the molecule makes nearly 90° with the azimuth of the other half.

Simon and Feher (1935) investigated the Raman spectrum of hydrogen peroxide at different concentrations in water ranging from 3 to 99·5% The H_2O band appeared even in the most concentrated solutions, indicating

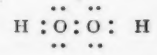
the linking H–O. A line at 887 cm.$^{-1}$ corresponded with the O–O vibration. A band at 1421 with two maxima 27 cm.$^{-1}$ apart, was observed for the first time. This was attributed to a deformation vibration corresponding with the valency angle between H–O and O–O. It practically disappeared below 30% H_2O_2. Another band at 3410 cm.$^{-1}$ was found to widen with dilution and split into maxima in 50% H_2O_2.

The investigations of Simon and Feher (1935) indicate that probably the relative proportions of the tautomeric forms in an aqueous solution of hydrogen peroxide depends on the concentration of the peroxide. This is indicated by the fact that the band at 1421, attributed to a deformation vibration corresponding to the valence angle between H–O and O–O disappears below 30% H_2O_2. The model of Penney and Sutherland (1934 *a*) seems to be more predominant at high concentrations than at low concentrations of H_2O_2.

Magnetic evidence obtained in the present investigation supports these conclusions strongly. Making full allowance for any errors in the values of the ionic susceptibilities it is found that the molecular susceptibility of hydrogen peroxide is intermediate between the values corresponding to the two structures proposed. The observed value is nearer the value calculated for the constitution



than for the constitution



thus being in complete agreement with Raman effect data.*

(*c*) *Sodium and barium peroxide.*—It was mentioned that the molecular susceptibility for Na_2O was $-19{\cdot}8$ and that of Na_2O_2 $-28{\cdot}1$. This indicates that the additional susceptibility due to the second oxygen is $-8{\cdot}3$.

In the case of barium, the molecular susceptibility of the monoxide is $-29{\cdot}1$ and that of the peroxide is $-40{\cdot}6$. The additional susceptibility due to oxygen is $-11{\cdot}5$.

The contribution to molecular susceptibility by the oxygen ion O^{-2} is $-13{\cdot}7$. If the oxygen is linked by a double bond, its contribution is only $-7{\cdot}7$ according to Kido.

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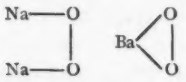
* *Note added in proof.*—Since fresh supplies of 30% H_2O_2 were not available, investigations at concentrations higher than 32% could not be carried out.

The values obtained above support the usual structures given, *viz.*,



The increase in susceptibility due to the oxygen over the basic oxide is just what one would expect for this oxygen. No large change takes place indicating any change of valency of the metal in the basic oxide. Thus the results of the present investigation show definitely that the valency of the metal is the same in the peroxide and monoxide.

Summary

The magnetic susceptibilities of hydrogen peroxide in water at different concentrations below 32% have been studied. Also peroxides of sodium and barium have been investigated.

The results obtained support the view that H_2O_2 exists in two tautomeric forms. It is probable that the relative proportions of the tautomeric forms depend on the concentration of the peroxide.

The susceptibilities of barium and sodium peroxides support the structure in which the oxygen atom is singly linked to the metal and to oxygen, thus preserving the valency of the metal in the basic oxide unchanged.

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THE USE OF FISH AS TEST ANIMALS FOR THE STUDY OF INSECTICIDES

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Some of the most noteworthy of modern insecticides of plant origin were originally used as fish-poisons by primitive tribes in various parts of the world. Consequently, the use of fish as test animals for insecticides is quite obvious. However, the method does not seem to have been so popular. Pittenger and Vanderkleed[1] were the first to employ this method and they found that gold-fish was a suitable test-animal for the assay digitalis preparations. Powers[2] and subsequently Gersdorff[3] used these fish for toxicological studies of other substances. The former observed in his experiments the death-point of the fish at which complete cessation of movements occurred, and he noted as the survival time, the time interval between addition of the fish-poison to the fish-tank and the death point of the fish. Plotting the survival times as ordinates against the concentrations of the test solutions as abscissæ, he obtained a curve which was logarithmic in function and whose middle portion approached an equilateral hyperbola. Further details of the calculation of toxicity are given in the paper of Gersdorff. According to them phenol, potassium cyanide and rotenone have respectively the toxicities 0·0008, 0·16, and 4. Surprisingly these values indicate that rotenone is 25 times as toxic as potassium cyanide and the latter is 200 times as toxic as phenol to fish.

More recently, in connection with their investigation on natural coumarins, Spaeth and his collaborators examined the effect of a number of synthetic and natural coumarins using tropical fresh-water fish, known as *Lebistes reticulatus* (Spaeth[4]). For purposes of comparison they noted the concentration of substances necessary for causing death within a time of 8 hours. This is obviously meant as a very rough comparison.

In the course of our work on insecticides, there was need for a rapid and reliable method for comparing the toxicities of natural and synthetic compounds. The procedure adopted by Spaeth and collaborators is not reliable, and details are lacking. The common time interval employed by them seems to be too long. In the procedure of Powers used subsequently also by

Gersdorff, the death-point was employed. We noticed that this is rather indefinite, however carefully the mouth and gill movements be followed. These movements persisted for a long time after the fish sank to the bottom. In some cases fish that were given up for dead came back to life in about an hour when removed to fresh water. Consequently some other criterion which is more well defined had to be sought for. As noted by Gersdorff, with toxic doses the activity of the fish gradually diminished and there was apparent difficulty to preserve equilibrium. Next they overturned and started swimming upside down and after a little while they sank to the bottom and lay on their backs. The stage at which they get overturned seems to be fairly definite and could be taken as a sign of toxicity. By using this point, there are several advantages; (1) there is definiteness in the record, (2) the period of the experiment becomes shorter and (3) the fish could be revived by transfer into fresh water and consequently could be used again for the experiments after the lapse of a few days.

When the above ' turning-point ' is employed as a criterion of toxic effect and the time interval plotted on a graph against concentrations of the solutions, a curve very similar to that of Powers is obtained, thus indicating that the new procedure yields results as valid as those of previous authors.

With a view to effect simplification in the technique, we have determined the concentration for each substance corresponding to a ' turning-time ' of 10 minutes. This interval has been chosen since with most substances the point falls within the ' hyperbolic ' portion of the curves and hence in the region where the time interval is inversely proportional to the concentration. Outside this portion of the curve the relation obviously does not hold good due to various factors that affect this biological property. Consequently the reciprocal of the concentration employed for each substance within this range gives a measure of its toxicity.

In order to facilitate comparison there is need for a standard and a system of expressing toxicity in terms of units. As the most easily available and the most well-known of insecticides, rotenone is chosen, and the standard preparation containing CCl_4 of crystallisation (B.D.H.) is employed. The toxicity is expressed as fish units and that of rotenone is arbitrarily fixed as 1000 ' fish-units '. This is a convenient number since otherwise the toxicities of other substances which are much weaker have to be expressed in terms of inconveniently small fractions.

The fish employed for these experiments have to be of the fresh-water type and they should be adapted to still water conditions. Gold fish come

under this category. A few varieties of fresh-water fish obtainable in the neighbourhood of Waltair were examined and among them one variety was found to be very suitable. These fish are very handsome and when fully grown measure about 1½ inches in length and weigh about 700–800 milligrams. They have been identified as *Haplochilus panchax*, a common larvicidal fish belonging to the family 'Cyprinodontidæ'. On an average six fish were employed for each experiment.

As the substances to be tested were almost insoluble in water, they were as a rule dissolved in alcohol and a measured volume of the solution poured into a measured amount of tap water. The amount of alcohol thus added was such that it usually did not exceed 1%, which according to blank experiments was not found harmful. A number of fish, usually six were placed in the solution and the turning point for each was recorded. The average for all the fish was taken as the 'turning-time'.

The actual procedure for the determination of the toxicity may be described as below. Using a number of concentrations the corresponding turning-times are observed and the results are plotted on a graph. From this graph, the concentration corresponding to 10 minutes turning-time is obtained and this is taken as the 'toxic concentration'. For rotenone it is found to be 0·2 mgm. per litre. Toxicity of a substance is proportional to the reciprocal of the toxic concentration. Consequently the following equation is obtained:

$$\frac{\text{toxicity of substance}}{\text{toxicity of rotenone}} = \frac{0{\cdot}2}{x}.$$

The toxicity (T) as defined above is then obtained from the following formula $T = \frac{0{\cdot}2}{x} \times 1000$ fish-uits (toxicity of rotenone) where x is the toxic-concentration of the substance. When plotting the results it could be seen if the 10 minutes interval falls in the region of sensitiveness. The results will not be quite reliable, if the point be far outside this limit.

The following table gives the results obtained in a few typical cases of organic compounds:

TABLE I

Name of Compound	Toxic Concentration in mgm. per litre	Toxicity in fish-units
(i) Rotenone ..	0·2	1000
(ii) Karanjin ..	6·6	30
(iii) Psoralen ..	38·5	5
(iv) Angelicin (Isopsoralen) ..	6·8	29

The number of compounds examined do not warrant any generalisation regarding the influence of chemical constitution on toxicity. But a probable inference is that pyronofuran derivatives of the angular type (i, ii and iv) are definitely more powerful as fish poisons than the linear type (iii). It is expected that by the adoption of the above procedure the toxicity determinations made by different workers and made with the use of other fish may not vary much. The values may be expected to be independent of these variations.

Experimental

Rotenone.—A standard solution of rotenone (10 mgm. in 50 c.c. of rectified spirits) using a sample supplied by B.D.H. was prepared. Measured volumes of this solution were added to different troughs, containing a measured amount of tap water (1 litre). The turning-points were determined in the case of six fish at each of these concentrations and the intervals of time elapsing between the commencement of the experiment and of the turning upside down of the fish were noted. At each concentration the mean of the time-intervals of the fish was calculated and the figure used in plotting the graph. The toxicity-curve thus obtained was a rectangular hyperbola (Table II).

TABLE II

Temperature of experiment : 31·5° C.

Concentration in mgm. per litre	Mean turning-time in minutes
0·065	75
0·130	26
*0·260	9·0
0·660	7·0
1·300	6·0

TABLE III

Strength of standard solution: 20 mgm. in 25 c.c. rectified spirits

Temperature of experiment : 32·0° C.

Concentration in mgm. per litre	Mean turning-time in minutes
2	125
4	17
6	11
*8	9·0
12	5·5

* With concentrations higher than the toxic concentration it is possible to measure turning-time correct to half a minute.

Toxic concentration from the graph: 0·2 mgm. rotenone per litre. This was confirmed experimentally as follows. To a trough containing 1 litre of tapwater, 1 c.c. of the above rotenone solution (1c.c. = 0·2 mg.) was added. Six fish were put into the trough and the mean turning-time determined; it was found to be in agreement with expectations (*i.e.*) 10 minutes.

In Table III are given the results obtained with karanjin, as another illustration of the method employed.

Toxic concentration from Graph is 6·6 mgm.

$$\text{Toxicity} = \frac{0{\cdot}2}{6{\cdot}6} \times 1000 = 30 \text{ fish units.}$$

Summary

A simple procedure employing fish is described for determining the toxicity of chemical compounds. The 'turning-point' is taken as the criterion of toxic effect and the toxicity is expressed in terms of fish units that of rotenone being arbitrarily fixed as 1000. A few organic compounds belonging to the group pyronofurans have been studied.

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